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XXXIX. *The Complexity of the Elements.*—Part II. *Elements of Even Atomic Number* *. *By* A. S. Russell, *M.A., D.Sc., Student and Tutor of Christ Church, Oxford* †.

§ 1. *Introduction.*

IN this paper I propose to develop a scheme for predicting the complexity of elements of even atomic number in the range $z=82$ to 36, making use of the principles and postulates of Part I. of this paper. The possible complexity of even elements will be dealt with first, in general terms; second, an attempt will be made to arrange the mass-numbers of the isotopes of many elements in the order in which they are considered to be in Nature; and third, the relation of mass-number to the stability of the nucleus will be discussed.

§ 2. *The Limits of the Mass-Numbers of Even Elements in the range* $z=82$ *to* 36.

Even elements may be considered in four groups—(1) simple elements, (2) complex elements without odd isotopes, (3) with one odd isotope, and (4) with two odd isotopes. An element of the first group has one mass-number, of the second two or three, of the third five, and

* Part I., Phil. Mag. vol. xlvii. p. 1121 (1924).

† Communicated by the Author.

of the fourth seven. This is arrived at in the following way :—

(*a*) It is assumed that the most complex inactive element has a difference in limit of mass-number of 8 units, has only two odd isotopes, and that the mass-numbers of these are neither the highest nor lowest of all. If all even mass-numbers are included between the limits, the element must have five even and two odd isotopes. Examples of this class are xenon (54) and tin (50). Their odd mass-numbers are numerically second and fourth lowest. This is considered to be typical of the class.

(*b*) A less complex class is regarded as obtained from the more complex class by discarding the two lowest isotopes. This class has consequently a difference in limit of mass-number of 6, four possible even isotopes and one odd, which is, in mass-number, second lowest. Mercury (80) with limits of mass-number of 198 and 204 is considered typical of this class.

(*c*) The next class, obtained from the one above in the same way as it was obtained, has a difference in mass-number of 4, and in consequence three even isotopes only. Special cases of this class are those with two and with one isotope only.

Even elements in the range $z=36$ to $z=82$ have already been divided into classes (2), (3), and (4), mentioned above in the earlier paper. Possibly complex elements without odd isotopes were given in the first column of Table IX.; those with one odd isotope in the second column of the same table, and those with two odd isotopes in the third column.

There are possibly one or more groups in the class without odd isotopes that are simple. The criterion of the simplicity of an element in absence of experimental evidence would be the possession of an atomic weight approximately an integer, and of the form $4k$, since all even simple elements according to Aston's work are of this form. In Table I. are arranged the groups of elements without odd isotopes and their atomic weights. It is seen that the only group which appears simple is the group $16n+10$, and it will be taken to be so in what follows.

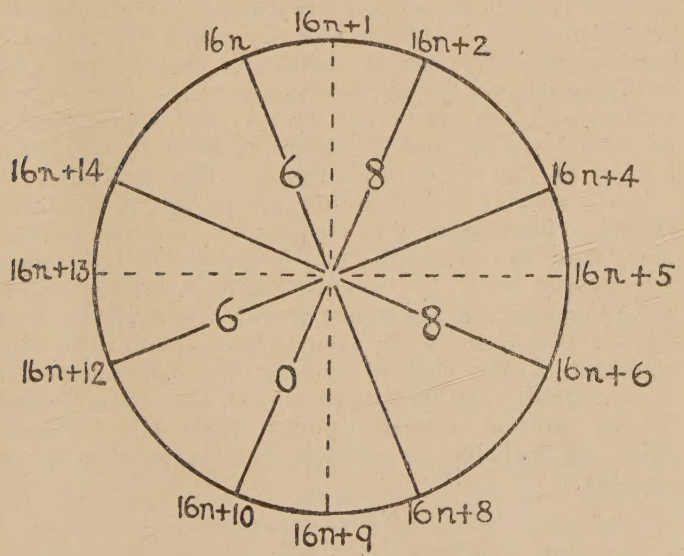
Of the eight groups into which the even elements may be divided in the range under consideration, the groups $16n$ and $16n+12$, having one odd isotope per element, have a range of mass-numbers of 6, $16n+2$ and $16n+6$ a range of 8, and the group $16n+10$ a range of 0, since

TABLE I.

Element.	Atomic weight.	Element.	Atomic weight.
Iron (26)	55·85	Zinc (30)	65·37
Molybdenum (42)	96·0	Palladium (46)	106·7
Cerium (58)	140·25	Samarium (62)	150·4
Tungsten (74)	184·0	Platinum (78)	195·2
Calcium (20)	40·06	Chromium (24)	52·0
Krypton (36)	82·92	Zirconium (40)	90·6
Tellurium (52)	127·5	Barium (56)	137·37
Erbium (68)	167·7	Hafnium (72)	?

it is likely to be simple. The ranges of the three others may be guessed at by making use of the diagram, fig. 1, which is very similar to fig. 1 of the earlier paper, and

Fig. 1.



illustrates the periodicity of the complexity of even elements in the range considered. The group-numbers $16n$, $16n+2$, etc. are arranged in order round a circle, and the difference in limits of their mass-numbers, where known, placed on their radii. As before, the lines joining $16n+1$ and $16n+9$ and $16n+5$ and $16n+13$ are the axes of symmetry. Each known limit on the right of the former

axis of symmetry is 2 greater than its corresponding limit on the left. It would follow, therefore, that the limit for the group $16n+8$ is 2, and those for groups $16n+14$ and $16n+4$, 0 and 2 respectively, or 2 and 4 respectively. Table II. sets forth these results more explicitly.

TABLE II.

Difference in limits of mass-number.	Atomic number of element.
8	82, 70, 66, 54, 50, 38, 34.
6	80, 76, 64, 60, 48, 44.
4	Possibly 68, 52, 36.
2	72, 56, 40, and possibly 68, 52, 36, 78, 62, 46.
0	74, 58, 42, and possibly 78, 62, 46.

§ 3. *Absolute Values of the Limits of Mass-Numbers of Complex Elements.*

It is, of course, possible that the assumptions which led to the above results are unnecessarily simple. It is interesting, therefore, to see if another line of inquiry will support or modify them. The likeliest method of attack appears to be a consideration of the absolute values of the limits of mass-numbers. These are known for the radio-elements 92, 90, 88, 86, 84, and 82, and for the inactive elements 80, 54, 50, 36, and 34, and will be made use of in this section.

A radioactive isobare is not usually the first or second isotope in importance of an element; it does not belong to more than two elements; and it appears to be connected numerically with the atomic numbers which share it according to a rule analogous to two mentioned in Part I. This is that if a_1 be an even isobare, z_1 and z_2 the atomic numbers of the element sharing the mass-number, and δ numerically the difference $a_1-(z_1+z_2)$, then δ applies to one pair of elements only. Table III. A illustrates this. It includes all radioactive isobares of even mass-number.

TABLE III. A.

δ.	z_1.	z_2.	a_1.	Radioactive products.
52	92	90	234	UX_1, U_{II}.
50	90	88	228	$MsTh_1$, Ra.
48	84	82	214	RaC', RaB.
46	84	82	212	ThC', ThB.
44	84	82	210	Po, RaD.

It has been pointed out by W. P. Widdowson and the

writer * that when an element has an odd isotope the limits of its mass-numbers are usually from 5 above the higher isotope (if there be two) to 1 below the lower. Since all odd isotopes belonging to even elements were deduced in Part I., the limits of all elements with odd isotopes are known if this rule be made use of. The limits of the other elements, however, are not known except those of the class $16n+10$ which is considered simple. The remaining limits may be obtained, however, if the isobare rule mentioned above be applied to inactive elements.

The results of doing the latter are included in Table III. B, and from the results of both parts of Table III., Table IV. is compiled.

TABLE III. B.

δ.	z_1.	z_2.	a_1.	Authority.
42	82	80	204	—
40	78	76	194	—
38	72	70	180	—
36	72	70	178	—
34	68	66	168	—
32	68	66	166	—
30	66	64	160	—
28	62	60	150	—
26	56	54	136	—
24	54	52	130	—
22	54	52	128	—
20	54	52	126	—
18	50	48	116	—
16	46	44	106	—
14	?	?	—	—
12	36	34	82	Aston.
10	36	34	80	Aston.
8	36	34	78	Aston.
8	34	32	74	Aston.
8	32	30	70	Aston.

It is seen in Table III. B that the isobare rule breaks down at the difference 8 which applies to no less than three sets of elements. In this respect it resembles the analogous rules referred to. No elements appear to correspond to the difference 14. If strontium had an isotope of 92, or krypton one of 88, or selenium one of 84, a pair of elements could be found for it; but the first two of these possibilities are unlikely, and there is no experimental evidence for the third. The gap arises owing to the anomalous value of the principal isotope of zirconium.

* W. P. Widdowson & A. S. Russell, Phil. Mag. xlviii. p. 293 (1924).

The expected value, as will be shown in the next section, is 94; the value of the atomic weight suggests strongly 90. If the higher value was the real one, strontium would be a complex element, though less complex than others of the class $16n+6$, and have an isotope 92 isobaric with one belonging to zirconium. But as zirconium's principal isotope is 90, strontium is limited to the isotopes

TABLE IV.

Element.	Limits of Mass-number.
U (92)	234–240
Th (90)	228–234
Ra (88)	224–228
Em (86)	220–222
Po (84)	210–218
Pb (82)	204–214
Hg (80)	198–204
Pt (78)	194–196
Os (76)	188–194 or 186–194
W (74)	—
Hf (72)	178–180 or 178–182
Yb (70)	172–180
Er (68)	166–168 or 166–170
Dy (66)	160–168
Gd (64)	154–160
Sa (62)	150–152
Nd (60)	144–150 or 142–150
Ce (58)	—
Ba (56)	136–138
Xe (54)	126–136
Te (52)	126–130
Sn (50)	116–124
Cd (48)	110–116
Pd (46)	106–108
Ru (44)	100–106 or 98–106
Mo (42)	—
Zr (40)	90–92 or 90–94
Sr (38)	—
Kr (36)	78–86

88 and 86, since it may not have a mass-number which is the principal mass-number of another element. The isobare rule excludes the second isotope, since the difference 12 is assigned to elements 36 and 34. Strontium * is consequently a simple element, as Aston finds.

In Table IV. are given some alternative possibilities

* If it were complex, the probability that its isotopes are 88 and 86 only is much greater than that of another possibility.

consistent with the data of Table III. They occur chiefly with elements in the neighbourhood of simple elements. Comparing the data of Table IV. with the limits assigned to the elements in Table II. the following points arise :—

(*a*) Elements 78, 62, and 46 are probably not simple but have two isotopes.

(*b*) Elements 72, 56, and 40 have probably each two isotopes only but possibly three.

(*c*) Elements 68, 52, and 36 have each probably three isotopes.

(*d*) Lead (82) has isotopes from 204–212 considered as a common element, and includes 214 as a radio-element. The mass-number 204 is demanded both by the isobare rule and also by the rule connecting limits with the values of odd isotopes.

(*e*) Xenon (54) has also apparently a range of 10, but the value 126 is demanded only by the isobare rule. If this isotope is genuine it is probably a "second-order" isotope for, as will be seen in § 5, it does not fit in with the other even isotopes of this element.

(*f*) Mass-numbers 186, 170, 142, 98, and 94 may be missing, but if not they are probably isotopes of minor importance of elements 76, 68, 60, 44, and 40 respectively.

§ 4. *Order of the Masses of Isotopes.*

Three things at least must be known before the masses of the isotopes of an element may even approximately be arranged in the order of their importance : (1) the chief even isotope, (2) the second even isotope, and (3) the relation between mass-number and stability. The second of these has been the most difficult to discover, and except in very easy cases I have not been able to find out how to calculate it. The third will be discussed in § 5 ; and the first now.

It is clear from Aston's results that the chief even mass-number of an element cannot be guessed at from the latter's atomic weight ; the more complex the element and the closer the masses of isotopes are, the more likely is such a guess to be in error. On the other hand, if an element has two isotopes only the relative importance of each may be easily ascertained.

The chief even isotope of an even element is related in many cases to the isotope or the lower isotope of the element next below it by the empirical rule that it is 5 or 3 units

greater according as the even element is complex or simple. The values of the odd isotopes are those predicted in Part I. Secondly, in many cases the value of the chief isotope ascends by 6 units from one even element to another when the latter is complex, and by 2 units when the latter is simple. Thirdly, in several cases the principal even isotope is three units above the

TABLE V.

Atomic Number.	Calculated Values. 1st Method.	2nd Method.	3rd Method.	Experimental.	Authority.
92	236	(238)	238	238	At.-wt.
90	232	232	—	232	At.-wt.
88	—	226	226	226	At.-wt.
86	—	220	222	222	Radioactivity.
84	214	214	—	210	Radioactivity.
82	208	208	208	206 or 208	Radioactivity.
80	200	202	202	202	
78	198	196			
79	190	190	192		
47	184	184	—	184	At.-wt.
72	182	182			
70	176	176	176		
68	170	170			
66	164	164	164		
64	156	158	158		
62	152	152			
60	146	146	148		
58	140	140	—	140	At.-wt.
56	138	138			
54	132	132	132	132	Aston.
52	126	126	—	128?	At.-wt.
50	120	120	120	120	Aston.
48	112	114	114		
46	108	108			
44	102	102	104		
42	96	96	—	96	At.-wt.
40	94	94	—	90	At.-wt.
38	88	88	—	88	Aston.
36	84	86	86	84	Aston.
34	80	80	80	80	Aston.
32	74	74	—	72	Aston.
30	68	68	—	64	Aston.
28	64	62	—	58	Aston.
26	60	56	—	56	Aston.

lower of its two odd isotopes when there are two, and three units above its odd isotope when there is one. The chief even isotopes derived in these ways are included in Table V., which contains also such experimental values as are known.

It is seen that the agreements are poor for elements below selenium (34), but that, in the range under consideration, they are, on the whole, good. Alternative experimental values of lead's (82) chief isotope have been given. Radioactivity favours the lower value; the atomic weight determination the higher. It has not yet been done by the positive-rays method. Outstanding discrepancies between the experimental and calculated values are seen in the principal isotopes of zirconium (40) and of polonium (84). In no case in the range considered are there more than two different values for the four results.

I have not been able to estimate by a general method the values of the second even isotopes.

§ 5. *Stability of the Nucleus a function of the Mass-Numbers of Isotopes.*

There are two relations in radioactivity known as Fajans' α-ray and β-ray rules which connect the mass-numbers of isotopes with the stability of their nuclei. The α-ray rule is that α-ray isotopes of ascending mass-number have periods in ascending magnitude; the β-ray rule that β-ray isotopes of ascending mass-number have periods in descending magnitude. To these empirical rules there are, as is well known, a few exceptions. The α-ray rule holds perfectly for the isotopes of elements 92, 90, and 86, holds partly for elements 88 and 84, and does not fail completely for any element. The β-ray rule holds perfectly for elements 89, 83, and 81, holds partly for element 82, but fails for element 90. Table VI. contains the data on which these statements are based. In this table it is assumed that actinuranium (AcU) is the head of the uranium series and the parent of uranium Y, the product of which is proto-actinium. This appears to me to be in better accord with present knowledge than the commonly-accepted view. This assumption, however, does not affect the validity of the empirical rules under discussion. The table includes also the assumed isotopes of the inactive elements bismuth and thallium.

TABLE VI.

Element.	Descending order of the periods of isotopes with their radiations and mass-numbers.					
Uranium (92)	U_I, (α); 238	AcU, (α); 235	U_{II}, (α). 234			
Protoactinium (91).	Pa, (α); 231	UX_2, (β); 234	UZ, (β). 234			
Thorium (90)	Th, (α); 232	Io, (α); 230	RdTh, (α); 228	UX_1, (β); 234	RdAc, (α); 227	UY, (β 231
Actinium (89)	Ac, (β); 227	$MsTh_2$, (β). 228				
Radium (88).....	Ra, (α); 226	$MsTh_1$, (β); 228	AcX, (α); 227	ThX, (α). 224		
Emanation (86) ...	Rn, (α); 222	Tn, (α); 220	An, (α). 219			
Polonium (84)	Po, (α); 210	RaA, (α); 218	ThA, (α); 216	AcA, (α); 215	RaC', (α); 214	ThC', (α 212
Bismuth (83)	Bi; 209	RaE, (β); 210	ThC, (β); 212	RaC, (β); 214	AcC, (α). 211	
Lead (82).....	RaΩ', (206) AcΩ'', (207); ThΩ', (208) RaΩ'', (210)	RaD, (β); 210	ThB, (β); 212	AcB, (β); 211	RaB, (β). 214	
Thallium (81)	Tl, (203); Tl, (205)	AcC'', (β); 207	ThC'', (β); 208	RaC'', (β). 210		

From the above table, however, two wider generalizations may be deduced and these, it will be shown, apply approximately also to the isotopes of inactive elements to the extent they have so far been experimentally determined. These are :—

I. In elements of old atomic number the isotope of lowest mass-number has the largest period.

II.(a) In elements of even atomic number the order of the periods of even mass-numbers is given by a clockwise arrangement of these mass-numbers. Going clockwise round the face gives an "ascending" series, and counter-clockwise a "descending" series.

(b) In an "ascending" series the odd mass-number is in its order of intensity when placed immediately before the mass-number three units greater.

(c) In a "descending" series the odd mass-number is in its order of intensity when placed immediately after the mass-number which is one greater when the series descends continuously ; and immediately after the highest mass-number when it does not.

It is seen from Table VI. that rule I. holds perfectly for all odd elements included in it. It is immaterial whether the isotope emit any radiation or not, or whether it be of even or of odd mass-number. The application of this rule to inactive elements has already been discussed in Part I. of this paper.

Rule II. is much less definite, and with the meagre data available it is difficult to know what, if any, is its bearing on the question of the stability of the nucleus. It is seen from Table VI., however, that the first part of the rule, II.(*a*), holds for all elements, for which data are available, except uranium ($z=92$). This element alone contains no product of another element as an isotope, and is consequently in an exceptional position. The rule would require mass-numbers for uranium of 238, 240, 234, and 236, or of 238, 236, 234, and 240 in descending order of period. The experimental evidence neither favours these possibilities nor is against them. It is possible that at a former epoch, or even now, one of them represents uranium †.

In Table VII. is seen how the rule applies to the isotopes of inactive elements. For these elements "relative concentration" must be substituted for "period." It is seen that the agreement is fair. Points where experimental work and the rule disagree are underlined.

Table VII.

Element.	Descending order of importance of masses.	
	Experimental.	According to Rule II.
Mercury (80)	202, $\left\{\begin{matrix}200\\198\end{matrix}\right\}$, 204*	202, 200, 198, 204
Xenon (54).....	132, 134, 136, 128, 130, 126, 124	132, 134, 136, 128, 130
Tin (50)	120, 118, 116, 124, 122	120, 118, 116, 124, 122
Krypton (36)	84, 86, 82, 80, 78	86, 84, 82, 80, 78
Selenium (34)	80, 78, 76, 82, 74	80, 78, 76, 82
Calcium (20)	40, 44	40, 44, 42
Argon (18).....	40, 36	40, 36, 38

* This arrangement is most consistent with Aston's results and with the accepted atomic weight.

† See also G. Kirsch, *Sitzb. Akad. Wiss. Wien*, vol. cxxxi. p. 551 (1922).

The rule does not give the minor isotopes of xenon or that of selenium. These lie outside the limits of mass-number for which it is operative, because from the number and value of the odd isotopes of these elements the limits of xenon are regarded as 128–136 and of selenium 76–82.

The exact relation of the relative concentrations of odd to those of even isotopes in an element of even atomic number is a more difficult problem. In "ascending series" like that of lead (82) (Table VI.) or of xenon (54) (Table VII.), odd isotopes are among the principal ones, and their position is given by rule II.(*b*) above. According to Fajans' β-ray rule an "ascending series" is a series of isotopes all of which expel β-particles, but the order of the isotopes of lead, the only even element that possesses such a series, is given better by rule II. than by the β-ray rule.

Most series, however, are "descending" series like those of thorium (90), mercury (80), and tin (50), and in these the odd isotope is of less importance and in some cases of minor importance Fajans' α-ray rule would demand that it be placed next below the mass-number one unit greater if the latter were an α-ray body. This rule generalized to exclude the provisoes of radioactivity holds (see Table VI.) for the positions of radioactinium (88), acton (86), actinium A (84), and for actinuranium (92) if uranium's second isotope has a mass-number 236. It would hold also for radioactinium (90) if the period of this body were greater than that of uranium X. (The periods are close, however, 19·5 days and 24·6 days respectively.) It fails to account for the position of uranium Y as does Fajans' β-ray rule also. Among the inactive elements it may apply to mercury's isotope of 199, but it does not apply to the odd isotopes of tin (50), krypton (36), or selenium (34). Rule II.(*c*), on the other hand, applies to the odd isotopes of uranium, thorium, radium, emanation, polonium, lead, tin, and selenium, might apply to that of mercury, and fails only for the isotope 83 of krypton. The experimental data in support of this are given in Table VI. above and in Table VIII. below.

Table VIII.

Element.	Descending order of intensities of isotopes.
Mercury (80)	202, 200, 199?, 198, 204, 199?
Tin (50)	120, 118, 116, 124, 119, 117, 122
Krypton (36)	84, 86, 82, 83, 80, 78
Selenium (34).....	80, 78, 76, 82, 77, 74

§ 6. *The Order of the Masses of Isotopes.*

The lack of knowledge regarding the second even isotope of an even element prevents a prediction of the order of the masses of isotopes for the complex elements, even when their number and absolute values have been estimated. This would not matter if one knew when a series of isotopes was an "ascending" or a "descending" one, but this is evidently not a periodic property since lead (82) has an "ascending" series and tin (50) a "descending" one. If dysprosium (66) has the former its order would be according to Tables IV., V., and rule II., 161, 164, 163, 166, 168, 160, 162 ; if the latter, 164, 162, 160, 168, 163, 161, 166. The atomic weight, 162·5, is consistent with either.

If ytterbium (70) has a series similar to xenon (54) its order would be similarly 173, 176, 175, 178, 180, 172, 174, and, if it has a "descending" series, it would be 176, 174, 172, 180, 175, 173, 178. The atomic weight, 173·5, is in favour of the former, but this may not be a very exact value. Cadmium (48) if "descending" should have 114, 112, 110, 116, 111, or 112, 110, 116, 114, 111 according as 114 or 112 is the principal even isotope, and, if "ascending," 111, 114, 116, 110, 112, or 112, 111, 114, 116, 110. The first and fourth of these are most probable, since neither 112 nor 114 is likely to be of minor importance. The atomic weight, 112·41, is not decisive but favours the first and third ; analogy with mercury (80) favours the first.

Others may be worked out in this way, but obviously an ambiguous answer may be given even when the principles laid down here are kept to strictly. The evidence of atomic-weight favours "ascending" series for ruthenium (44) and for neodymium (60), the former commencing on the mass-number 100, the latter on 144 ; it favours also "descending" series for osmium (76) and for gadolinium (64), the former commencing on the mass-number 192, the latter on 158. The elements without odd isotopes appear easier : platinum (78) is likely to have isotopes of 196 and 194 only ; hafnium (72) 180 and either or both of 182 and 178 ; erbium (78) 170, 168, 166 ; samarium (62) 152 and 150 ; barium (56) 138 and 136 ; tellurium (52) 126, 128, 130 ; palladium (46) 106 and 108, and zirconium (40) 90 and 92. Tungsten (74), cerium (58), molybdenum (42), and probably strontium are simple.

Summary.

(1) The complexity of the elements of even atomic number between selenium and lead is investigated on the lines employed in Part I.

(2) The number of isotopes and their mass-numbers are calculated for each element in the range investigated on the assumption that the complexity of the elements is a function of the atomic number 16 and by making use of empirical relations that apply equally to radioactive isotopes and to those of ordinary elements.

(3) A generalization similar to, but wider than Fajans' α- and β-ray rules for the order of the masses of isotopes is stated, and is found applicable both to radioactive isotopes and to those of ordinary elements so far experimentally investigated.

(4) With the help of this generalization an attempt is made to predict the order of the masses of isotopes of many elements still to be examined by the positive-ray method.

Dr. Lee's Laboratory,
Christ Church, Oxford.
May 1923.

XL. *The Selection Principle: A Development based upon the Stokes-Thomson Pulse Theory.* *By* C. N. Wall*.

THE selection principle which states that the azimuthal quantum number can change at most by unity in any interorbital transition of an electron is due to Rubinowicz *. Bohr † has also deduced a restricted selection principle which excludes a zero change in angular momentum. A rigorous development of this principle demands extensive knowledge of the classical electrodynamics and vector analysis. However, this principle may be deduced very simply though with less rigour by basing the deduction upon the Stokes-Thomson pulse theory for an electron and certain ramifications of this theory.

Consider the changes which take place, according to the quantum theory of electronic orbits, when an electron such

* Communicated by Prof. Jakob Kunz.

* Rubinowicz, *Phys. Zeit.* xix, pp. 441 and 465 (1918); Sommerfeld, *Atombau*, 3d Ed., pp. 310–339 and Appendix.

† Bohr, "Quantum Theory of Line Spectra," Pts. I. and II., Danish Academy of Science.

as in an ion of helium undergoes an interorbital transition and radiates light. In such a transition the electron loses a certain amount of energy, namely, $\Delta E = E_1 - E_2$, where E_1 represents the total energy of the electron in its initial orbit and E_2 the total energy in its final orbit. This loss of energy is radiated in the form of electromagnetic waves whose frequency ν is given by the relation

$$\Delta E = h\nu,$$

where h is Planck's constant. In addition to the loss in energy the electron suffers a certain change in angular momentum, $\Delta P = |P_1 - P_2|$, where P_1 and P_2 designate respectively the angular momentum of the electron in its initial and final orbit. It is assumed that this change in angular momentum suffered by the electron in its transition is carried away by its radiation, so that both energy and angular momentum are conserved. In other words, the radiation emitted by the electron in its interorbital transition contains within itself both the energy and the angular momentum given up by the electron in its transition. The plausibility of such an assumption as the conservation of angular momentum is greatly strengthened if one remembers that circularly polarized light should contain both energy and angular momentum *.

It is necessary to determine the relation between ΔE and ΔP. In order to do this we make use of the classical theory of electrodynamics and work with what may be termed the equivalent path of an electron in the classical theory, or what is sometimes referred to as a vibration ellipse of an electron. In short, we make the assumption that an electron jumping from an initial orbit to a final orbit according to the quantum theory is in a sense equivalent in classical electrodynamics to an electron undergoing simple harmonic notion of frequency ν along two perpendicular axes X and Y with amplitudes a and b respectively and a phase difference of $\pm \frac{\pi}{2}$. Thus the vibration electron has an ellipse as its orbit with semi-axes a and b. The coordinates of this vibration or equivalent electron in its vibration or equivalent path at any instant t are evidently

$$\left.\begin{aligned} x &= a \cos 2\pi\nu t \\ y &= b \sin 2\pi\nu t. \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (1)$$

* Poynting, 'Collected Scientific Papers,' pp. 372–379.

Its velocity components are

$$\left.\begin{aligned} x' &= \frac{dx}{dt} = -a2\pi\nu \sin 2\pi\nu t, \\ y' &= \frac{dy}{dt} = b2\pi\nu \cos 2\pi\nu t. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

The acceleration components are

$$\left.\begin{aligned} x'' &= \frac{d^2x}{dt^2} = -a(2\pi\nu)^2 \cos 2\pi\nu t, \\ y'' &= \frac{d^2y}{dt^2} = -b(2\pi\nu)^2 \sin 2\pi\nu t. \end{aligned}\right\} \quad . \quad . \quad (3)$$

As this so-called vibration electron moves around its elliptical orbit it radiates both energy and angular momentum according to the classical theory. Furthermore, by hypothesis the relation between this radiated energy and angular momentum is identical with the relation between ΔE and ΔP. Thus it is only necessary to determine the relation between the energy and the angular momentum radiated by a vibration electron in one or more complete vibrations.

Sir G. Stokes first suggested that an electron suffering an impulse would send out an electromagnetic pulse emitted at the instant of the impulse. Sir J. J. Thomson * calculated the energy radiated by such an electron, and Larmor extended the theory to the case of an accelerated electron. It may easily be shown † by this theory that the rate of radiation of energy from an electron accelerated along the X-axis is given by

$$\left(\frac{dE}{dt}\right)_x = \frac{2e^2}{3c} x''^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where e represents the electronic charge, c the velocity of light, and x''^2 the square of the acceleration of the electron along the X-axis. A similar equation may be written for acceleration along the Y-axis. A more rigorous analysis ‡ of the problem leads to the conclusion that expression (4) is not accurate if one desires to compute the rate of radiation of energy from an accelerated electron at any special instant. However, the total emission of radiation through a sufficiently

* J. J. Thomson, Phil. Mag. xlv. p. 172 (1898).

† J. A. Crowther, 'Ions, Electrons, and Ionizing Radiations,' pp. 143–147.

‡ Jeans, 'Electricity and Magnetism.' Sec. 649, 4th Ed.

large interval of time is accurately given upon integrating the expression through this time interval. Fortunately it is in this sense that we are going to use the expression.

Suppose now that we look upon this radiation by an accelerated electron as implying the existence of a reactive force acting upon the electron. If F_x and F_y represent the components of this reactive force due to radiation then obviously the following equations must hold,

$$\left.\begin{aligned} F_x x' &= \frac{2e^2}{3c} x'^{\prime 2}, \\ F_y y' &= \frac{2e^2}{3c} y'^{\prime 2}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By means of these equations it is possible to calculate the values of F_x and F_y. It must not be inferred, however, that the above values of F_x and F_y represent the total reactive forces acting upon the electron. F_x and F_y are only the non-conservative forces acting upon the electron due to the friction-like effect of energy radiation. There are certain conservative forces which also act upon the electron. If all these forces are taken into consideration then it has been shown by Lorentz* that the total reactive force upon the electron should be directly proportional to the first derivative of the acceleration of the electron. Nevertheless, in determining the value of the energy and the angular momentum radiated by the vibration electron in any integral number of whole vibrations a time integral around the entire ellipse is required, so that the energy and angular momentum contributed by the conservative reactive forces acting upon the electron vanish for such an integration and the non-conservative reactive forces alone furnish the value of the integral. Accordingly the same result is obtained if one uses the total reactive force on the electron.

The next task is to set up expressions for both the energy and the angular momentum radiated by the vibration electron during any integral number of complete vibrations. Evidently the total energy radiated during n (positive integral number) complete vibrations is given by the expression

$$E_n = \int_0^{\frac{n}{\nu}} (x' F_x + y' F_y) dt. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

* Lorentz, 'The Theory of Electrons,' p. 251.

The total angular momentum radiated for n complete vibrations is given by the expression

$$P_n = \int_0^{\frac{n}{\nu}} (xF_y - yF_x)dt. \quad . \quad . \quad . \quad . \quad (7)$$

Let us multiply equation (6) through by the constant $k = \frac{2ab}{a^2+b^2}\frac{1}{2\pi\nu}$ and subtract the resulting form from equation (7). We have

$$\left.\begin{aligned} P_n - kE_n &= \int_0^{\frac{n}{\nu}} \Big[(xF_y - yF_x) - k(x'F_x + y'F_y)\Big]dt \\ &= \int_0^{\frac{n}{\nu}} \Big[F_x(-kx' - y) + F_y(-ky' + x)\Big]dt. \end{aligned}\right\} \quad (8)$$

If now we substitute in the right-hand member of expression (8) the values of F_x and F_y as determined in equations (5), and then make the further substitutions for x, y, x', y', x'', and y'', as determined in equations (1), (2), and (3), the integrand simplifies considerably. Upon carrying out the indicated integration the right-hand member vanishes for all positive integral values of n. Thus we obtain the relation

$$P_n = kE_n = \frac{E_n}{2\pi\nu}\frac{2ab}{a^2+b^2}, \quad . \quad . \quad . \quad . \quad (9)$$

which gives the relation between the energy and angular momentum radiated by the vibration electron in n complete vibrations.

By taking the finite differences of P_n and E_n with respect to n we get at once

$$\Delta P = \frac{\Delta E}{2\pi\nu}\frac{2ab}{a^2+b^2}. \quad . \quad . \quad . \quad . \quad (10)$$

In accordance with our assumptions this relation deduced by classical methods is the relation between the change in energy and angular momentum of an electron undergoing an interorbital transition. But for such a transition

$$\Delta P = |P_1 - P_2| = \frac{h}{2\pi}|m_1 - m_2|,$$

since

$$P_1 = \frac{m_1 h}{2\pi} \quad \text{and} \quad P_2 = \frac{m_2 h}{2\pi},$$

m_1 and m_2 being respectively the azimuthal quantum numbers for the initial and final orbits. Also $\Delta E = h\nu$.

Therefore expression (10) becomes after these substitutions

$$|m_1 - m_2| = \frac{2ab}{a^2 + b^2}. \quad . \quad . \quad . \quad . \quad (11)$$

In short, we arrive at expression (11) by quantizing the classical relation (10).

Now

$$2ab \leqq a^2 + b^2 \quad \text{since} \quad (a - b)^2 \geqq 0.$$

Therefore

$$|m_1 - m_2| \leqq 1.$$

Since by the quantum theory m_1 and m_2 must be positive integers it follows that the difference between m_1 and m_2 can only be ± 1 or zero, *i.e.* we have the three cases

$$\left.\begin{aligned} m_1 - m_2 &= +1, \quad a = b \text{ since } \frac{2ab}{a^2 + b^2} = 1, \\ m_1 - m_2 &= -1, \quad a = b \text{ since } \frac{2ab}{a^2 + b^2} = 1, \\ m_1 - m_2 &= 0, \quad a = 0, b = 0, \text{ or } a = b = 0. \end{aligned}\right\} \quad (12)$$

The relations (12) give at once the essence of the principle of selection : the azimuthal quantum number can change at most by unity in any interorbital transition of the electron. The polarization rule follows immediately : if the azimuthal quantum number changes by ± 1 the light emitted because of an interorbital transition will be circularly polarized ; otherwise, there will be linear polarization.

In conclusion it might be well to point out that the development of the selection principle depends upon the quantizing of a relation developed by the use of classical electrodynamics. It states that only those interorbital transitions are possible in the quantum theory in which the accompanying changes of energy and angular momentum are compatible with the classical theory. In this sense the principle of selection serves as a bond which tends to tie together more closely the quantum theory and the classical theory.

Thanks are due to Professor Jakob Kunz for valuable suggestions in the preparation of this paper.

Laboratory of Physics,
University of Illinois,
Urbana, Illinois,
November, 1923.

XLI. *Quantum Defect and Atomic Number.* *By* Louis A. Turner, *M.A., Ph.D., Charlotte Elizabeth Procter Fellow in Physics, Princeton University* *.

THE values of the terms of a series of spectroscopic terms are given by the expression

$$\frac{N}{\{m+a+f(m)\}^2},$$

where N is the Rydberg constant, m has different integral values for the different terms with a value of 1 for the first, a is a constant, and $f(m)$ is a function of m, of which the numerical value is small compared with a and decreases rapidly with increasing m. For the hydrogen spectrum $a=0, f(m)=0$, and the values of m are, according to Bohr's theory, the principal quantum numbers of the corresponding electron orbits. By analogy, the denominator of the more general expression for a term is called the effective quantum number of the term. If n be the actual principal quantum number of the orbit corresponding to the term, and $m+a+f(m)$ the effective quantum number, the difference $q=n-\{m+a+f(m)\}$ is called the quantum defect. As n is taken larger and larger m increases by the same amount, but $f(m)$ diminishes rapidly so that q approaches a limiting value $n-m-a$ which equals some small integer minus a.

The order of magnitude of q depends upon which of the two possible types of orbit the one in question belongs to. Bohr † calls them orbits of the first kind and orbits of the second kind. Orbits of the first kind are those in which the valence electron remains throughout the orbit completely outside of the region traversed by the inner electrons of the atomic structure. I have discussed elsewhere ‡ a possible interpretation of the difference between the values of the terms corresponding to such orbits for the alkali metal atoms and the ionized atoms having a structure similar to that of Na. The q values for such orbits are small fractions. Orbits of the second kind are those in which the electron penetrates the region

* Communicated by Prof. K. T. Compton.

† N. Bohr, *Annalen der Physik*, lxxi. p. 228 (1923).

‡ Louis A. Turner, Astrophys. Journ. lviii. 3. p. 176 (1923), and lix. 4. p. – (1924).

traversed by the other electrons and passes close to the nucleus during part of the orbit. For such orbits q may have a value of several units. For an electron of given energy and angular momentum the contribution to the integral $\oint p_r dr$, which gives the radial quantum number, will be much greater during that part of the orbit when it is close to a nucleus of several units positive charge than it would be for that same part of the orbit in a coulomb field of a single positive charge. The effective or apparent quantum number will therefore be less than the actual one.

If this theory be correct, we should expect that the limiting value of the quantum defect for series of the same type should be a function of the nuclear charge—*i. e.*, of the atomic number. The purpose of the present paper is to point out certain empirical relations of this kind and their bearing upon the theory of atomic structure. The values of the constant a have for the most part been taken directly from the series formulas or calculated from the term values given in Professor Fowler's Report on Series in Line Spectra. In addition, constants calculated by Fowler*, Fues†, and Datta ‡, and data for Sr given by Saunders § and for Al^+ given by Paschen ‖, have been used. It should be pointed out that a takes practically the same value, no matter what form of $f(m)$ is used in the computation. The data for the different types of spectra are presented and discussed separately, and followed by a more general discussion.

Doublet Spectra of the Alkali Metal Type.

Table I. gives the values of the constant a for the series of the second kind in the spectra of the alkali metal type. The quantum numbers given are those of the largest term of the series, first, as given by Bohr¶ in his theory of atomic structure, and second, as the following work seems to indicate that they should be. There are two corresponding values of the quantum defect.

* A. Fowler, Proc. Roy. Soc. A, ciii. p. 413 (1923).
† E. Fues, *Ann. d. Phys.* lxiii. p. 21 (1920).
‡ S. Datta, Proc. Roy. Soc. A, xcix. p. 71 (1921).
§ F. A. Saunders, Astrophys. Journ. lvi. p. 73 (1922).
‖ F. Paschen, *Ann. d. Phys.* lxxi. p. 537 (1923).
¶ N. Bohr, *loc. cit.*

TABLE I.—Doublet Spectra.

Element.	Atomic Number.	Series.	a.	Quantum Numbers (Bohr).	q.	Quantum Numbers (L.A.T.).	q.	$q_s - q_p$.
Li	3	s	0·60	2_1	0·40	2_1	0·40	0·35
		p_1	0·951	2_2	0·049	2_2	0·049	
Na	11	s	0·650	3_1	1·350	3_1	1·350	0·50
		p_1	1·148	3_2	0·852	3_2	0·852	
K	19	s	0·822	4_1	2·178	4_1	2·178	0·48
		p_1	1·296	4_2	1·704	4_2	1·704	
Rb	37	s	0·87	5_1	3·13	6_1	4·13	0·50
		p_1	1·366	5_2	2·634	6_2	3·634	
Cs	55	s	0·95	6_1	4·05	8_1	6·05	0·50
		p_1	1·449	6_2	3·551	8_2	5·551	
Cu	29	s	0·42	4_1	2·58	5_1	3·58	
Ag	47	s	0·49	5_1	3·51	7_1	5·51	
Mg^+	12	s	0·934	3_1	1·066	3_1	1·066	0·37
		p	1·305	3_2	0·695	3_2	0·695	
Ca^+	20	s	1·201	4_1	1·799	4_1	1·799	
		d''	1·36	4_3	1·64	4_3	1·64	
Sr^+	38	s	1·315	5_1	2·685	6_1	3·685	
		d''	1·52	5_3	2·48	6_3	3·48	
Ba^+	56	s	1·430	6_1	3·570	8_1	5·570	
		d''	1·58	6_3	3·42	8_3	5·42	
Ra^+	88	s	1·33	7_1	4·69	11_1	8·69	
Zn^+	30	s	0·35	4_1	2·65	5_1	3·65	
Cd^+	48	s	0·45	5_1	3·55	7_1	5·55	
Al^{++} ...	13	s	1·10	3_1	0·90	3_1	0·90	0·30
		p_1	1·40	3_2	0·60	3_2	0·60	
Si^{+++} ...	14	s	1·228	3_1	0·772	3_1	0·772	0·26
		p_1	1·492	3_2	0·508	3_2	0·508	

Fig. 1 shows the values of q for series in the neutral atoms plotted against the atomic numbers. If the values of q for the p_1 series of the alkali metal atoms obtained by the use of Bohr's quantum numbers be plotted, they lie along a broken line ABC, which changes slope at the K point. If, however, the value of q for Rb be increased by 1, and that for Cs by 2, the straight line ABD passes through the upper four points, the Li point falling slightly above the line. This would seem to indicate that the largest p_1 term of Rb has the quantum numbers 6_2 instead of 5_2 as given by Bohr, and that the largest p term of Cs has the quantum numbers 8_2 instead of 6_2.

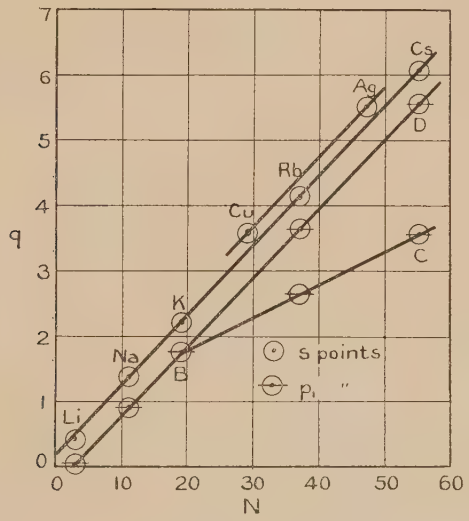
The reasons which make me believe that the present data call for this change are :—

1. If the general theory which accounts for the quantum defect of such orbits is correct, a continuous change with

increasing atomic number would be expected. That it should be a linear relation is surprising, but some sort of a smooth curve would be expected.

2. If a break of the line exists, because of the change of structure occurring in the long periods of the periodic arrangement of the elements, one would not expect the break to occur at the K point. This point would belong to one or the other segment of the line, but not to both, for the K atom must have one or the other structure, and not both.

Fig. 1.



3. It would be a remarkable coincidence if the change of slope were a real one, and yet such that the second line could be swung into the first by this precise integral change in the ordinates of the two points.

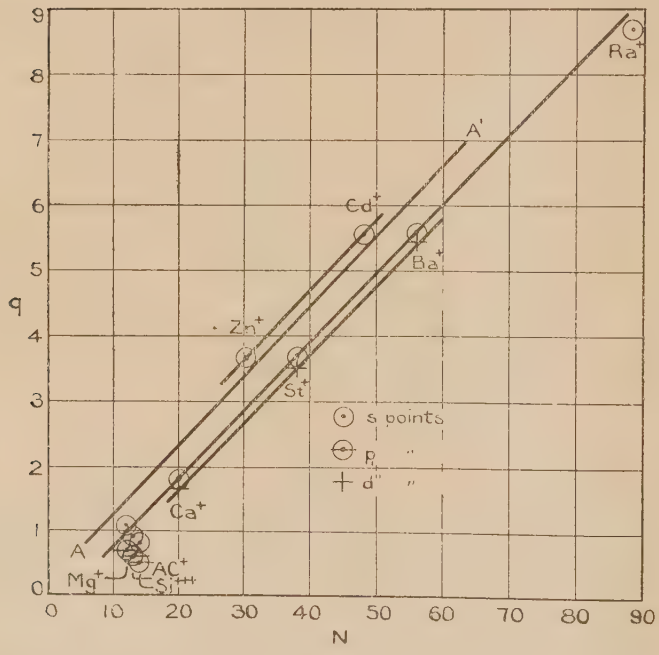
4. The same change produces the same result with other series, as will appear in the sequel.

The corresponding changes have been made in the quantum numbers from which the q's for the s terms of the alkalies have been calculated. Quantum numbers have been assigned to the Cu and Ag terms so as to bring the two points as close to the s curve for the alkalies as possible. They are 5 and 7 respectively, the two numbers fitting in between the value of 4 for K, 6 for Rb, and 8 for Cs. The equation of the p_1 line is $q = 0{\cdot}1068N - 0{\cdot}322$. The slopes of the other two lines are

approximately the same. The p_1 line for the alkalies lies a distance of 0·50 below the s line, as is apparent from the values of $q_s - q_p$. The two Li points do not fall very exactly on the lines. This is in agreement with Bohr's statement that the degree of penetration is different for Li.

The nth s or p_1 term in the spectrum of an alkali metal is less than the corresponding term in the spectrum of one of lower atomic number. A d or f term is larger, however. Hence quantum defects calculated for the d and f series could not fit into this scheme, for they do not increase the same way.

Fig. 2.



The orbits corresponding to these terms are apparently orbits of the first kind with quantum numbers as given by Bohr.

On fig. 2 are plotted the data for the spectra of this type given by ionized elements. The quantum numbers used correspond to those used for the data of fig. 1. The line AA′ is the s line of fig. 1 drawn in so that the two figures can be compared. The orbits for the d terms are apparently orbits of the second kind for elements of atomic number

higher than that of Ca. The Ra^+ point is not accurately determined because of the lack of sufficient data, but the deviation from the line is probably more than can be accounted for by this error. The Zn^+ and Cd^+ points show a considerable deviation from the alkaline earth metal line, but lie on a line nearly parallel to the others. The points corresponding to ionized elements lie below the lines for the neutral elements of the same spectroscopic type, the distance below being greater the greater the degree of ionization. The $q_s - q_p$ separation becomes less the greater the degree of ionization.

Triplet Spectra.

Table II. gives the available data for the triplet spectra of the divalent metals and also of O, S, and Se. Fig. 3 shows

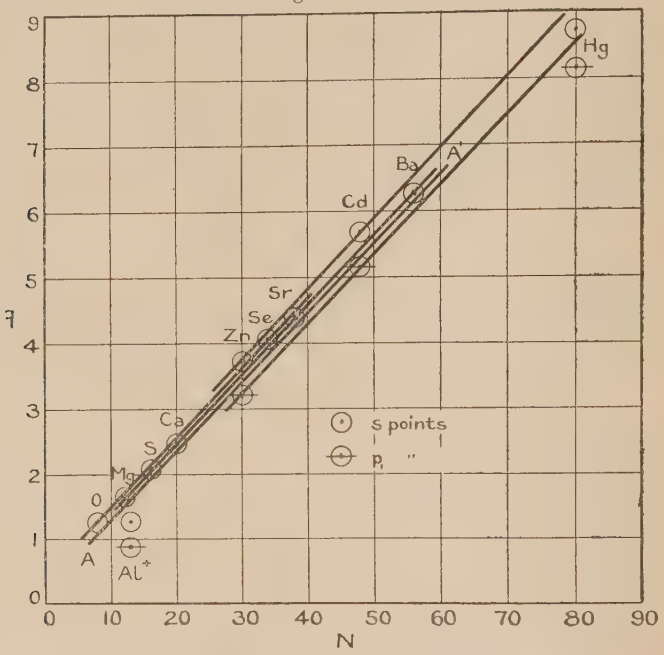
TABLE II.—Triplets.

Element.	Atomic Number.	Series.	a.	Quantum Numbers.	q.	$q_s - q_p$
Mg	12	s	1·377	4_1	1·623	
Ca	20	s	1·561	5_1	2·439	
Sr	38	s	1·631	7_1	4·369	
Ba.....	56	s	1·73	9_1	6·27	
Zn.....	30	s	1·28	6_1	3·72	0·52
		p_1	0·80	5_2	3·20	
Cd	48	s	1·33	8_1	5·67	0·53
		p_1	0·86	7_2	5·14	
Hg	80	s	1·29	11_1	8·71	0·59
		p_1	0·88	10_2	8·12	
O	8	s	0·77	3_1	1·23	
S	16	s	0·93	4_1	2·07	
Se	34	s	0·96	6_1	4·04	
Al^+	13	s	0·73	3_1	1·27	0·38
		p	1·11	3_2	0·89	

the lines obtained by plotting these data. The line AA′ is again the s line from fig. 1. It should be noted that the three s lines of fig. 3 for the different groups of elements all come very close to that of the alkali metals. The Hg point does not fall on any of these lines, but comes very close with the quantum number taken as indicated. The $q_s - q_d$ separations for Zn and Cd are 0·52 and 0·53, in fair agreement with the value of 0·50 for the alkalies. This value of 0·52 might be used to predict the wave-numbers of some of the higher p terms of the spectra of the alkaline earth metals.

The d terms of these spectra show unusual departures from the simple term formula, so that no values of a have been

Fig. 3.



computed. The Hg point falls considerably below the Zn–Cd line.

Singlet Spectra.

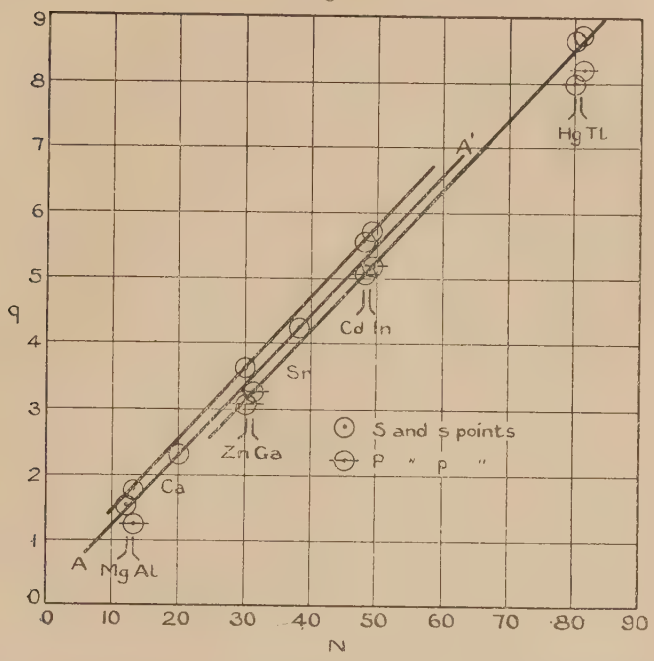
Table III. gives the data for the singlet series. These

TABLE III.—Singlets.

Element.	Atomic Number.	Series.	a.	Quantum Numbers.	q.	$q_s - q_p$.
Mg	12	S	0·47	3_1	1·53	
		P	—			
Ca	20	S	0·65	4_1	2·35	
		P	—			
Sr	38	S	0·74	6_1	4·26	
		P	—			
Ba	56	S	—			
		P	—			
Zn	30	S	0·35	5_1	3·65	0·56
		P	0·91	5_2	3·09	
Cd	48	S	0·41	7_1	5·59	0·53
		P	0·94	7_2	5·06	
Hg	80	S	0·36	10_1 (?)	8·64	0·63
		P	0·99	10_2	8·01	

data are plotted in fig. 4. Again the S line comes very close

Fig. 4.



to that for the alkali metals (AA'), the P line falls a distance of about 0·55 below it, and the Hg points are too low.

Doublet Spectra, Al type.

Table IV. gives the data for these series. They are plotted

TABLE IV.

Metal.	Atomic Number.	Series.	a.	Quantum Numbers.	q.	$q_s - q_p$.
Al	13	s	1·22	4_1	1·78	0·53
		p_1	0·75	3_2	1·25	
Ga	31	s	—			—
		p_1	0·72	5_2	3·28	
In	49	s	1·27	8_1	5·73	0·53
		p_1	0·80	7_2	5·20	
Tl	81	s	1·25	11_1	8·75	0·58
		p_1	0·83	10_2	8·17	

in fig. 4 also. Again the S line comes very close to all the others. The $q_s - q_p$ differences are again 0·53 for Al and In,

but the difference for Tl is 0·58, and the Tl point falls below the line. The difference for Al^+ is 0·38.

Discussion.

Apparently any orbit of the second kind can be arbitrarily divided into three parts—one, where it is completely outside of the region of the other electrons and in a field very nearly the same as that of a single positive charge; another, where it is close to the nucleus in a much stronger field ; and the third transition part of the orbit when it is passing from one to the other. During this transition the particular structure of the atom will have its greatest effect. The fact that these S lines for the different elements and their different spectral types come so close together, seems to show that this quantum defect depends primarily upon the nuclear charge, and only to a slight extent upon the distribution of electrons in the outer parts of the atom—that is, the general course of the lines depends upon some very fundamental general relation of the electron to the nucleus, but their positions are shifted somewhat for the different outer electron structures. This point of view is in agreement with the changes in the quantum defect for the larger terms corresponding to smaller orbits. For these orbits the influence of the particular structure is of greater influence. This is specially true for the divalent atoms, where the second valence electron is presumably relatively loosely attached, and for which the terms show the greatest deviations from any of the simple series formulas.

The chief problem presented by these relations is the explanation of the linear relationships and the slope of the lines. That I have not been able to solve. The quantum defect for a given orbit is the excess of the contribution to the integral $\oint p_r dr$ which is made as the electron passes close to the nucleus over what it would have been had the electron remained in the field of a positive charge at a point. The decrease in quantum defect for ionized atom terms would be expected, because this contribution to the integral which must be subtracted is greater the greater the value of the net charge. The problem of calculating how much of a complete orbit the electron traverses in the region of the nucleus, and the contribution to the integral, is a very complicated one, even on the basis of the simplest reasonable assumptions.

If these relationships mean anything at all, we have to face

the alternative of either explaining the sharp break in the curve for quantum defect as a function of atomic number of all of these groups of similar spectra, or of altering the theory of atomic structure in its explanation of the details of the building-up of the atoms through the long periods. For the reasons given above, I think that the latter is necessary. The kernel of Rb will have to contain some orbits of principal quantum number 5 and that of Cs some of numbers 6 and 7. More spectroscopic information must be had before the details of the process can be worked out.

Regardless of the theoretical explanations, these relations should prove useful in working out series in the spectra of the elements ionized to different degrees. The same linear relationships will hold presumably, for they do so for the ionized alkaline-earth series. The parallelism of these lines brings out the fact that the difference between the constants a for two different series of terms is nearly constant for all elements of the same chemical sub-group. In particular, the difference of 0·50 to 0·55 between q_s and q_p for these neutral atoms of different spectroscopic type is worthy of note. I have never seen that fact explicitly pointed out, although it may have had something to do with the use of the values 1·5, 2·5, etc. for m in the formulas for the s series. This difference $q_s - q_p$ is, of course, equal to $a_p - a_s$. Perhaps the values for this difference of 0·37, 0·30, and 0·26 as obtained from the Mg^+, Al^{++}, and Si^{+++} spectra will be common to the spectra of various elements corresponding to these successive stages of ionization. The value of 0·38 for the Al^+ spectra lends support to that expectation. The fact that the four numbers 0·52, 0·37, 0·30, and 0·26 are in the ratio $1 : 2^{-\frac{3}{2}} : 3^{-\frac{3}{2}} : 4^{-\frac{3}{2}}$ may be of significance.

Mention should be made of the work of Brackett and Birge *, who discovered similar relationships. They plotted values of the effective quantum number of the various spectroscopic terms as a function of the number of electron groups beneath the valence electron as given by Bohr's theory. Lines were drawn through the points having the same quantum number according to that theory. They also found that corresponding parts of these curves had the same slope, especially for the terms of higher quantum number, and that there were certain recurring differences in these effective quantum numbers for different elements of different groups related similarly in the periodic arrangement. The present arrangement gives these results, and, in addition, gives a

* F. S. Brackett and R. T. Birge, Jour. Op. Soc. Am. viii. p. 213 (1924).

better correlation of elements of the same chemical group, and brings out more clearly the fundamental regularities common to all.

Summary.

1. It is found that by increasing Bohr's quantum numbers for the valence electrons of elements of atomic number greater than 28, limiting quantum defects can be computed which are linear functions of the atomic number, for corresponding series, for elements of the same chemical sub-group.

2. The slopes of these lines are all very nearly the same.

3. The s lines for elements of different chemical nature come very close together, indicating that the quantum defect depends primarily upon the atomic number and secondarily upon the particular atomic structure.

4. The p lines for all the neutral elements lie approximately 0·50 below the s lines, which means that the constant α in the term formula is 0·50 greater for p terms than for s terms for a given element.

5. The quantum defects for the series of ionized atoms are less than those of the corresponding neutral atoms.

6. The difference between the s and p quantum defects becomes less for higher degrees of ionization.

7. The regularities introduced by the increases of Bohr's quantum numbers indicate a possible need for a revision of the theory of the building-up of the atoms of the long periods of the periodic arrangement.

I wish to thank Professor K. T. Compton for his interest and helpful criticism of this work.

Princeton, New Jersey,
March 5, 1924.

Note.—Professor H. N. Russell has pointed out to me that straight lines will also be obtained if the quantum defects obtained from Bohr's quantum number are plotted against a sequence of integers. For example, one can use for abscissas for Li, 1 ; Na, 2 ; K, 3 ; Rb, 4 ; Cs, 5. There is no choice between the two methods of plotting on the basis of more accurate satisfaction of the linear relationship for either method. If this be the correct expression of the relationship, it means that the effect of the completion of each group of orbits corresponding to a whole chemical period has the same effect on the quantum defect, even though some of these

groups contain 8 electrons and others 18 or 32. It does not seem probable to me that these groups, so different in number, would influence the quantum defect by the same amount. One advantage of the scheme of changed quantum numbers is that it is in accord with the occurrence of simple spectra in elements in the middle of the longer periods, where the orbits of the next higher total quantum number begin to appear ; *i. e.*, if the quantum number of the normal orbit in K is 4, and that of Rb is 6, the intermediate number 5 is in all probability the correct one for the intermediate element of similar spectroscopic type, Cu. The change of 3 units between the quantum numbers of Ba and Ra would lead one to expect two elements with spectra of their type in the period of 32. Hg is one of these, of course. Hicks * has recently pointed out that lines of the spectrum of Eu indicate that it, too, is of this spectroscopic type. The more complete working out of the spectra of the rare earth elements will throw much light on this question.

XLII. *The Rotating Earth as a Reference System for Light Propagation.* *By* L. Silberstein, *Ph.D.*†

THE relativistic physicist has no difficulty in placing an "observer," with clock and measuring rod, now upon a distant star, now upon an atom or an electron, and reasoning about his experiences. There is certainly nothing illegitimate or contemptible about such fictitious standpoints or reference frames, provided they are helpful in deducing some consequences of a verifiable nature. Yet all such frames or reference systems offer only an indirect interest, and their properties cannot, of course, be explored without the intercalation of a chain of more or less uncertain principles, assumptions, or guesses. There is, however, one frame which can be explored directly and to which, moreover, all our actual observers are chained down, perhaps forever,—and that is our own Earth. The purpose of this paper is to emphasize the need for its experimental investigation as a reference system, especially for optical phenomena, and to state the actual problem without prejudice either against or in favour of Einstein's theory of relativity.

* W. M. Hicks, 'Nature,' 113. p. 642, May 3, 1924.

† Communicated by the Author. Paper read in the H. A. Lorentz Colloquium held at the University of Wisconsin, Madison, March 30, 1922. Communication No. 212 from the Research Laboratory of the Eastman Kodak Company.

The properties of the Earth as a reference frame for *mechanical phenomena* can be said to be fairly well known. They are anisotropic and symmetrically distributed around an axis practically fixed in the frame, and are typified, say, by the Foucault pendulum, the gyrocompass, and the projectile, whose behaviour is described, for the present at least, with sufficient accuracy by the well-known Newtonian equations of motion written for "rotating axes." If r be the position vector of a particle, these equations are condensed in the vector equation, in obvious symbols,

$$\left(\frac{d}{dt}+\mathrm{V}\tilde{\omega}\right)^2\mathbf{r}=\mathbf{F}$$

or, developed,

$$\ddot{\mathbf{r}}=\mathbf{F}-2\mathrm{V}\tilde{\omega}\dot{\mathbf{r}}+\omega^2\mathbf{r}-\tilde{\omega}(\tilde{\omega}\mathbf{r}), \quad . \quad . \quad . \quad . \quad (1)$$

where $\tilde{\omega}$ is a constant vector along the said axis of symmetry (SN) and ω its absolute value. Historically, of course, this equation was derived from $\mathbf{r}'=\mathbf{F}'=\mathbf{F}$, written for an inertial, say the fixed-stars system S', by the familiar relation $\mathbf{r}'=\mathbf{r}+\mathrm{V}\tilde{\omega}\mathbf{r}$, with $\tilde{\omega}$ as the spin vector of the Earth relative to S', or by the transformation of the cylindrical coordinates $z'=z$, $\rho'=\rho$,

$$\theta'=\theta+\omega t, \quad t'=t. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But once in possession of equation (1), we may as well forget its origin and look upon it intrinsically, from a purely terrestrial point of view. It then becomes meaningless, of course, to speak of the Earth's "rotation" (without adding relatively to what). The constant $\tilde{\omega}$ in (1) is then simply an ascertainable physical directed magnitude belonging to the Earth as such, considered as a reference frame for mechanical phenomena. That the same vector $\tilde{\omega}$, with reversed sign, happens to express also the revolution of the starred sky around us (whenever we choose to look up to it), is a most welcome addition to its terrestrial properties, which, however, does not concern us at this stage of the discussion. Of the two supplementary terms in (1) the first, normal to the Earth's axis and the particle's velocity, is known as "the Coriolis force," and the remaining two, amounting together to a transversal vector away from the axis of size $\omega^2\rho$, as "the centrifugal force," per unit mass. Thus far the Earth as a mechanical frame.

Our experimental knowledge of the planet as a reference system for *optical phenomena* is, thanks to the famous Michelson-Morley experiment, on the one hand perhaps of a

much more precise nature than the aforesaid, but on the other hand essentially less complete. It can be said without unfairness that what we know about it is just one-half of what seems worth knowing, or just as much as remains to be explored. The information derived from the Michelson-Morley experiment seems as fragmentary as would be our knowledge of the terrestrial mechanical frame if it were limited to experiments of short duration and extending over small distances *, and what remains to be found out would be the optical counterpart of the behaviour of gyrocompasses and long-range projectiles. In fact, what we have learned from the much discussed and extremely fruitful nil-effect of the Michelson-Morley experiment, stripped of every theoretical interpretation, can be stated as follows:—Let O, A, B be three points marked on a slab of stone †. Then, whatever the phase-difference or time-lag between the light-signalling $OAAO$ and $OBBO$ in one orientation of the slab, it remains the same for any other orientation, say, after turning the slab by 90°, relatively to the Earth, that is, and no matter at what season of the year. I purposely abstain from calling the slab a "rigid" body. For this would virtually amount to begging the question, and frustrate the desire of stating the result as one of purely phenomenal content divested from every interpretation. For the same reason no mention is made of the possibility of the "distance" OA or OB being "shortened" in a certain ratio (Lorentz contraction), whenever the segment is brought by a 90° rotation to a certain otherwise remarkable direction ‡. In fine, the experiment teaches us that there is no privileged direction, that the orientation of the slab is irrelevant. What is responsible for this monotonous, isotropic behaviour is a further question which, at this stage at least, does not interest us.

This, then, is the knowledge of the Earth as an optical reference frame we do possess.

Now, to pass at once to what we do *not* know about it, consider 1, 2, 3, three non-collinear fixed terrestrial stations. Let two light signals be sent simultaneously from 1, one to 2, thence to 3 and back to 1, the other to 3, thence to 2 and back to 1, mirrors being placed at 2 and 3 so as to avoid delay at the stations. The plain question is: *Will both*

* The former compared with $2\pi/\omega$, the day, and the latter with the radius of our planet.

† The support of the interferometer, to be sure, with OA and OB roughly "equal" and perpendicular to each other.

‡ That of the resultant of our orbital motion and of the motion of the solar system towards Hercules.

signals return to 1 *at the same time or not*? And if not, how does the time-lag of one behind the other depend on the circumstances of the experiment, the geometrical properties, the geographic position (presumably only the area and the geographic latitude, respectively), and the inclination of the plane of the triangle 123 to the horizon? It may be interesting to remark that the existence or non-existence of such a time-lag,

$$\Delta = t_{1231} - t_{1321},$$

important on its own account, has also an immediate bearing upon the fundamental question of the possibility of setting up on Earth a consistent clock synchronism based on light signalling, as first proposed by Einstein (1905). For the synchronism thus defined will be *transitive* *, if and only if $\Delta = 0$ for every optical circuit.

A reliable and definite answer to these questions can be obtained only from experiment, on a somewhat large scale. Preliminary experiments to that purpose have actually been started by Prof. Michelson at Passadena in 1921 and are still in progress. Their results, however, may not be available before the end of the summer of 1923 or, perhaps, of the succeeding year.

Theoretically, two different ways of conjecturing the possible outcome of these experiments offer themselves, one based upon the assumption of an æther, the other based upon Einstein's relativity theory, more especially upon the rôle attributed expressly by its founder to the world-geodesics and the minimal lines. With this proviso, the latter method will be shown to lead to a perceptibly definite, unique answer, while the former will give a whole range of possible values of the time-lag, for a given terrestrial optical circuit.

Let us first consider the problem on the æther theory. Without dwelling upon a number of details concerning the shape of light-rays, terrestrial optical trigonometry, etc., which together with the bibliography of the subject were given in a previous paper (Journ. Opt. Soc. of America, v. 1921, pp. 291–307), we may pass at once to the formula covering the only feasible experiment, that is to say, giving the time-lag Δ for an optical circuit. If $-\kappa\tilde{\omega}$ be the relative angular

* That is to say, the synchronism of clocks at 1 and at 2, and clocks at 2 and at 3, will entail the synchronism of those at 1 and 3. Needless to say that Einstein postulated this transitivity only for inertial systems, and would by no means expect it to hold for the Earth. The subject is here presented as it would be viewed by a radical experimentalist:—Given a reference frame, it is a matter-of-fact question whether an optically established synchronism of its clocks is or is not transitive.

velocity of the æther and the Earth near its surface (so that $\kappa - 1$ will be the rotatory dragging coefficient), σ the area of, say, the triangular circuit, and ω_n the component of the spin vector $\tilde{\omega}$ normal to its area, then the required time-lag is

$$\Delta = \frac{4\sigma\kappa\omega_n}{c^2}, \quad \ldots \ldots \quad (3)$$

where c has its usual meaning. As far as our knowledge goes, the numerical coefficient κ may have any value between 0 and 1. This formula can be easily deduced in a variety of ways. One of these, adopted by the writer (*l. c.* p. 299), is based upon the obvious (approximate) formula

$$\Delta = -\frac{1}{c^2}\int \mathbf{v}\,d\mathbf{l},$$

already noticed by Professor Lorentz *, where $d\mathbf{l}$ is a line-element of the light-path and $\mathbf{v}$ the relative velocity of the æther, in our case $\mathbf{v} = \kappa V\mathbf{r}\tilde{\omega}$. The application of Stokes's theorem gives then (3) at once. Another deduction, which has seemed interesting as being independent of the "ray" or "light-path" concept, is this. For simplicity consider a rotating disk, or a horizontal platform at the north pole. With the centre of rotation O as origin let r_1, r_2 be the radii vectores of two stations 1, 2, and θ the included angle. Let a light signal start from 1 at $t=0$. This will spread in the æther as a spherical wave (with the æther point 1 (0) as centre), which will reach the second station, *i. e.*, the æther point $2(t)$ at an instant t such that ct is the third side of the triangle $1(o)O2(t)$. Thus, rigorously,

$$c^2t^2 = r_1^2 + r_2^2 - 2r_1r_2\cos(\theta + \kappa\omega t),$$

a transcendental equation for the required time of passage $t = t_{12}$. In our case, $\kappa\omega t$ being in all practicable experiments a very small angle, this gives at once, up to ω^2 terms,

$$ct_{12} = D_{12} + r_1r_2\sin\theta\,.\,\frac{\kappa\omega}{c},$$

where $D_{12} = \overline{12}$. Similarly, $ct_{21} = D_{21} - r_2r_1\sin\theta\,.\,\frac{\kappa\omega}{c}$.

Whence,

$$t_{12} - t_{21} = \frac{4\kappa\omega}{c^2}\sigma(012), \quad \ldots \ldots \quad (4)$$

where the last factor is the area of the triangle 012. Treating

* *Wissenschaftliche Abhandlungen*, vol. i. p. 466.

similarly the pair of stations 2, 3, and so on, and adding up the time differences, we shall obtain the previous result with σ equal to the whole area embraced, no matter whether 0 is inside or outside the polygon of stations *.

Returning to formula (3), divide both sides by T, the period of oscillation. Then the phase delay per period, or the corresponding shift of the interference pattern with the fringe width as unit, will be

$$\epsilon = \frac{4\sigma\kappa\omega_n}{c\lambda}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

A sufficient description of the technicalities of the actual experiment will be found in the paper mentioned above. Here it will be enough to recall that for $\sigma = 1$ km.^{2}, $\lambda = 5000$Å., and for an angle of 45° between the normal of the triangle plane and the Earth's axis (say, for a horizontal circuit at Chicago), the shift would amount to

$$\epsilon = 1{\cdot}38\kappa, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

i. e., in the extreme case, of no drag, to about 1·4 fringe widths per each km.^{2} embraced by the circuit. (For Pasadena $\epsilon = 1{\cdot}095\kappa$.) As to the factor κ, it would be idle to speculate about its value. If there is no rotational drag, then $\kappa = 1$, if there is a full drag, $\kappa = 0$, and if a partial one, κ may have any intermediate value. If we are at all to return to the æther concept, then to account for the nil-effect of the Michelson-Morley experiment (which in distinction from the new or *rotational*, may appropriately be referred to as the *translational* terrestrial optical experiment) an almost complete translational dragging of the æther at the Earth's surface must be assumed. In fine, we must have recourse to the Stokes-Planck compressible æther to which Prof. Lorentz devoted an interesting investigation †. But from the translational or annual drag, should it even be complete, no inference can be drawn with regard to a rotational or daily drag of the æther by our planet. Direct data on daily

* Notice in passing that in the transition formula (4) of this proof the area (012) could easily be made enormous, even with the actual stations 1 and 2 not far apart (say only 100 metres at the equator). Unfortunately, however, $t_{12} - t_{21}$ cannot be made the object of precise measurement (and is even conceptually ill-defined), unlike $t_{12} + t_{21}$ which is t_{121}, a local process. This is the reason why at least *three* non-collinear stations (*i.e.*, not eclipsing each other) are indispensable.

† *Cf.* Columbia Lectures on 'The Theory of Electrons,' Chap. v. and *Abhandlungen*, vol. i. p. 454. In connexion with recent developments, see also my paper on "Recent Eclipse Results and Stokes-Planck's Æther," Phil. Mag. xxxix. Feb. 1920.

aberration, which might throw some light upon this question, are as good as absent, while from Lodge's and Sagnac's experiments, even if they were unimpeachable, one could judge only that there is no æther drag by their comparatively light turn-tables, but not by such massive bodies as the Earth. In fine, as far as is known, the whole interval from 0 to 1 is open to the coefficient κ, and its values may even turn out to be different at different places of the Earth's surface.

Let us now consider the same problem from the standpoint of modern Relativity. Notice that on the classical or Newtonian theory there is no definite connexion, and, in fact, no binding connexion whatever between the properties of the Earth (or any other frame) as a mechanical or kinetical reference system and its properties as a frame for optical phenomena. This is most emphatically shown by the mechanical equation (1) as contrasted with the optical formula (5), the former being perfectly definite, while the latter * is vague in very wide limits, as broad at least as the range of possible κ values. More generally, there is in Newtonian physics essentially no connexion between mechanics and optics.

In fine, no matter how precise our knowledge of the Earth as a mechanical frame, it leaves us completely in the dark with regard to its behaviour as an optical reference frame, on the classical theory. Not so on the relativity theory, in which optics and kinetics are intimately tied to each other. In fact,—and this is perhaps the most characteristic feature of Einstein's theory,—whatever the quadratic differential form determining the metrical properties of a world domain, its geodesics prescribe the motion of free particles, and the minimal lines of *the same metrical manifold* express the propagation of light in vacuo. In other words, if ds, given by the form

$$ds^2 = g_{\iota\kappa} dx_\iota dx_\kappa,$$

is the appropriate "line-element" for the description of the motion of free particles relatively to any frame S, through the corresponding geodesics

$$\delta \int ds = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

then *the same line-element* rules also the propagation of light in that system, through the minimal lines

$$ds = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(B)}$$

* Even apart from the new æther constant c and the independent introduction of that hypothetical medium at all.

It may, for instance, be very hard to find, for an actual reference frame, the appropriate ds. But if this be once found, it does both services at the same time: it characterizes the frame as both a mechanical and an optical reference system. The moral of this characteristic feature of Einstein's theory for the case under consideration is obvious.

In fact, the kinetical behaviour of the terrestrial frame is represented with sufficient accuracy by the equation (1) or by the expressions for the centrifugal and the Coriolis forces therein contained. To cover these by the world geodesics substantially, *i. e.* apart from terms immeasurably small, it is imperative to use for the line-element in terrestrial coordinates the form *

$$ds^2 = \left(1 - \frac{\omega^2 r^2}{c^2}\right) c^2 dt^2 - dr^2 - r^2 d\theta^2 - \frac{2r^2\omega}{c} d\theta \,.\, cdt, \quad (6)$$

which is simply the galileian line-element

$$ds^2 = c^2 dt'^2 - dr'^2 - r'^2 d\theta'^2$$

transcribed from the system S' to terrestrial co-ordinates by means of the transformation (2). The second-order term $\omega^2 r^2/c^2$ has been retained only to show this origin of (6). The question of the derivability of the coefficients (g_{ik}) of the quadratic form (6) as the solutions of Einstein's field-equations from huge masses revolving around our abode need not detain us here †. Enough that the form (6) with ω equal, of course, to our *full* angular velocity, 2π/day, is essentially indispensable for the correct description of terrestrial kinetics by means of the geodesics (A). Needless

* It is enough to consider here the two-dimensional case, with $dz=0$, that is. The gravitation of the Earth may be altogether disregarded, as its chief effect is only to modify the coefficients of the quadratic terms dt^2 and dr^2, which is without influence on the rotational optical experiment. The only effect upon a terrestrial optical circuit would be represented by a term amounting, at the utmost (at the equator), to $\frac{8}{5}\frac{M}{c^2 R}$, to be subtracted from the factor 2 in the last (rectangular) term, R being the radius and M the mass of the Earth in astronomical units. Since, however, $M/c^2 = 0{\cdot}45$ cm., this term is of the order 10^{-9}.

† Thirring's attempt at obtaining it is certainly unsatisfactory. According to Einstein's own admission (in a private conversation), the correct values of the centrifugal and the Coriolis force can only be obtained by accepting his cosmological hypothesis of a closed space and uniform mass distribution throughout it. The rotation of the whole universe around us will then give the desired result.

to explain that the approximation we have here in mind corresponds to putting in the final result, $ds \doteq cdt$. With this approximation the variation δr yields at once, by (A),

$$\frac{d^2r}{dt^2} = r\left(\omega + \frac{d\theta}{dt}\right)^2,$$

which exhibits the centrifugal acceleration. Similarly, the variation of θ will give the Coriolis term.

Now, such being the ds required for kinetic purposes, the optical aspect of the terrestrial frame will be completely determined by the principle (B), *i. e.*, dropping the term $r^2\omega^2/c^2$ which was kept only for formal reasons, by the equation

$$c^2dt^2 - \frac{2r^2\omega}{c}\, d\theta \,.\, cdt = dl^2, \quad . \quad . \quad . \quad . \quad (7)$$

where $dl = (dr + r^2d\theta^2)^{\frac{1}{2}}$ is the distance of two terrestrial stations. We need not even solve this equation, etc. in order to see that it leads to all results obtained from the æther-point of view, with $\kappa = 1$. For we know beforehand that it was obtained from the S' equation by the transformation $\theta' = \theta + \omega t$. Thus, for instance, light-rays, straight in S', will be spiral shaped for terrestrial observers, and so on. (Some curiosities will be found in the paper quoted before.) Thus also the previous shift formula, with $\kappa = 1$, must follow. In fact, (7) gives, up to second-order terms,

$$cdt = dl + r^2d\theta \,.\, \frac{\omega}{c},$$

which is identical with the previous formula for ct_{12}, for infinitesimal θ. Whence, as in (4),

$$dt_{12} - dt_{21} = 2r^2d\theta \,.\, \frac{\omega}{c^2} = \frac{4\omega}{c^2}\, d\sigma,$$

where $d\sigma$ is the area of the triangle 012.

Thus also the time-lag or corresponding fringe shift for any optical circuit, replacing for the general case ω by ω_n,

$$\epsilon = \frac{4\sigma\omega_n}{c\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

as in (5), but with the particular value $\kappa = 1$. Such then is, to a sufficient degree of approximation, the result to be expected on the relativity theory.

There is thus a possibility for discriminating, through the rotational terrestrial optical experiments now conducted by

Michelson, between the relativity- and an æther theory. To state the situation more precisely, if the result of these experiments will be a full shift effect ($\epsilon = 1{\cdot}38$ per km.^{2}, reduced to the stated conditions), there will be no discrimination between the two theories, but this being only one more evasive answer to all questions put to Nature in the name of the æther, it will certainly not help the exiled medium. Should there be, however, either *no* ascertainable shift at all or only a *fraction* κ of the "full" effect, sensibly smaller than unity *, the relativity theory will be (as Einstein himself gladly admitted) irremediably disproved, while on the æther theory one would have only to assume a complete or partial spinning drag of that medium. This gives the new terrestrial experiment a strong additional interest. As a matter of fact, it was the proof of this possibly crucial nature of the experiment by means of which the writer was fortunate enough to induce Prof. Michelson † to undertake it in spite of the technical difficulties. After what has been explained, it is scarcely necessary to say that by "relativity theory" is here meant the doctrine such as was given to us by Einstein and, if modified, then certainly not so as to give up the concrete (physical) interpretation of either the world-geodesics or the minimal lines. The beauty and conceptual value of Einstein's work as an abstract theory will persist even in the extreme unfavourable case of a nil-effect.

But apart from all such considerations of a possible crucial test, and whatever the final result (nil, fractional, or a full shift), it will undoubtedly be a very desirable contribution to our knowledge of the planet as an optical or electromagnetic system of reference.

Research Laboratory, Eastman Kodak Company,
Rochester, N.Y.,
March 15, 1923.

* Prof. Michelson, who up to the time of this colloquium was not able to discern less than 0·05 of a fringe width, has recently succeeded in pushing this threshold of observability down to 0·01, although the fixing of the "zero" by the control circuit (*cf. loc. cit.*) is thus far somewhat less precise. [In the meantime, November 1923, also the "zero" was fixed by Prof. Michelson to within $\pm 0{\cdot}013$ of a fringe width.]

† Who as early as 1904 discussed it on the æther theory. *Cf.* first paper.

XLIII. *Electron Theory of Aberration and Lorentz Transformations.* *By* Dr. D. N. Mallik, *F.R.S.E., Sc.D., Professor of Physics, Aligarh Muslim University, Aligarh, India* *.

1. In the usual development of the electron theory of aberration (as given by Poincaré and others), while it enables us to deduce Fresnel's dragging coefficient, it supplies no clue to the Lorentz transformations as a necessary consequence of that theory. In the present paper these transformations are derived as a necessary consequence of the electron theory.

2. Whatever view we may take regarding the physical existence of an æther †, we have to admit, in the present state of science at any rate, that a moving electron produces a magnetic *field*. If this is granted, we should be justified in regarding the total energy in the Langrangian sense as made up of that of the electrons themselves and that of the field. This procedure was adopted in a paper "On the Theory of Dispersion," in Phil. Mag. April 1915, and, as will be presently shown, directly leads to all the results.

3. Let T_1 = Kinetic energy of an electron,
T_2 = that of the associated magnetic field, which may provisionally be taken to be that of the æther,
V_1 = Potential energy due to extraneous forces,
V_2 = Potential energy of the æther.

Then, if x, y, z define the position of an electron,

$$\frac{d}{dt}\frac{dT_2}{d\dot{x}} = -\frac{d}{dt}\int(\beta h - \gamma g)\,d\tau,$$

since

$$-\int(\dot{\beta}h - \dot{\gamma}g)\,d\tau = \text{momentum of the field},$$

where (α, β, γ) = magnetic force, (f, g, h) = electric polarization, and $d\tau$ = an element of volume.

* Communicated by the Author.

† With regard to this, the latest pronouncement of Larmor ('Proceedings of the Cambridge Philosophical Society,' vol. xxi. part iv.) may be quoted:—

"... as is here claimed, closer scrutiny compels a reversion to the view that space is a plenum, is an æther in the historical and ultimate British sense, ... not a coherent scheme of local physical relations. ..."

But

$$\int\left(h\frac{\partial f}{\partial z}+g\frac{\partial f}{\partial y}\right)=-\int f\left(\frac{\partial f}{\partial x}+\frac{\partial g}{\partial y}+\frac{\partial h}{\partial z}\right)d\tau=-\int f\rho\,d\tau$$

and (remembering $4\pi\omega=\frac{\partial\beta}{\partial x}-\frac{\partial\alpha}{\partial y}$, &c.)

$$-4\pi\int(\beta\omega-\gamma u)\,d\tau=\int\alpha\left(\frac{\partial\alpha}{\partial x}+\frac{\partial\beta}{\partial y}+\frac{\partial\gamma}{\partial z}\right)d\tau$$
$$+\frac{1}{2}\int\frac{\partial}{\partial x}(\alpha^2+\beta^2+\gamma^2)\,d\tau\text{ (by integration by parts)}=0,$$

since
$$\frac{\partial\alpha}{\partial x}+\frac{\partial\beta}{\partial y}+\frac{\partial\gamma}{\partial z}=0$$

and surface integrals necessarily vanish when taken over the entire field.

Thus
$$\frac{d}{dt}\frac{\partial T_2}{\partial\dot{x}}=-\frac{4\pi}{k_0}\int f\rho\,d\tau-\int\rho(\gamma\dot{y}-\dot{z}\beta)\,d\tau.$$

Moreover,

$$\int\frac{\partial T_2}{\partial x}d\tau=\frac{1}{8\pi}\int\frac{\partial}{\partial x}(\alpha^2+\beta^2+\gamma^2)\,d\tau=0,$$

and
$$\frac{2\pi}{k_0}\int\frac{\partial}{\partial x}(f^2+g^2+h^2)\,d\tau=\frac{\partial V_2}{dx}=0$$
$$\left[\frac{1}{\sqrt{k_0}}=\text{velocity of light in the æther}\right].$$

Now the Langrangian equation of motion is of the type

$$\frac{d}{dt}\left(\frac{\partial T_1}{\partial\dot{x}}+\frac{\partial T_2}{\partial\dot{x}}\right)-\frac{\partial(T_1+T_2)}{\partial x}+\frac{\partial(V_1+V_2)}{\partial x}=0\ ;$$

i. e.,
$$\frac{d}{dt}\left(\frac{\partial T_1}{\partial\dot{x}}\right)+\frac{\partial V_1}{\partial x}=\frac{4\pi}{k_0}\int f\rho\,d\tau+\int(\rho\dot{y}-\beta\dot{z})\,d\tau$$

if we admit $\frac{\partial T_1}{\partial x}=0$, *i. e.* regard electrons to be of invariable size.

Now $T_1=\frac{1}{2}(Le^2+m)(\dot{x}^2+\dot{y}^2+\dot{z}^2)$ for a single electron

of self-inductance L, mass m, and charge e, while

$$-\frac{\partial V_1}{\partial x} = \text{force due to system of electrons in a given volume} + \text{force brought into play on account of displacement } (x-x_0, \text{ \&c.}) \text{ of the electrons,}$$

$$= \frac{4}{3}\pi\frac{A}{k_0} \text{ per unit charge (as in the corresponding magnetic theory) } -\lambda(x-x_0) \text{ (per unit charge).}$$

$$= \frac{4}{3}\frac{\pi}{k_0}\int A\rho\, d\tau - \lambda\int\frac{A}{\rho}\rho\, d\tau \text{ (where } \lambda \text{ is a constant for a small displacement)}$$

since $$\rho(x-x_0) = A,$$

where A, B, C are defined by

$$\frac{\partial A}{\partial x}+\frac{\partial B}{\partial y}+\frac{\partial C}{\partial z} = -\rho$$

$$= -\left(\frac{\partial f}{\partial x}+\frac{\partial g}{\partial y}+\frac{\partial h}{\partial z}\right),$$

i. e., I (A, B, C) is the coefficient of electrification, giving rise to electronic moment $I\,d\tau$.

4. For the entire system of electrons in volume $\int d\tau$, we have, accordingly, equations of the type

$$\frac{1}{e}\int(Le^2+m)\,\ddot{v}\rho\, d\tau + \frac{\lambda}{e}\int A\, d\tau - \frac{4}{3}\frac{\pi}{k_0}\int A\rho\, d\tau$$

$$= \frac{4\pi}{k_0}\left[\int \rho f\, d\tau + \rho(\gamma\dot{y}-\dot{z}\beta)\,\delta\tau\right].$$

Writing $\rho\ddot{v} = \ddot{A}$, and taking mean values of the various quantities under the sign of integration, viz.

$$\frac{\int \ddot{A}\, d\tau}{\int d\tau} \equiv \ddot{A}, \frac{\int(A+3f)\,d\tau}{\int d\tau} \equiv e(A+3f), \quad \text{\&c.},$$

we have

$$(Le^2+m)\,\ddot{A}+\lambda A = \frac{4\pi}{k_0}e^2\{(\tfrac{1}{3}A+f)+(\dot{y}\gamma-\dot{z}\beta)\},$$

which can be written in the form

$$\ddot{A}_k + p_k^2 A_k = a_k f$$

if the magnetic effect is omitted or is nil, the suffix referring to the kth group of electrons.

5. Again, the expression for the energy (as was shown in the former paper) can also be written for *a material medium*,

$$W = \frac{2\pi}{k}\int (f_0^2 + g_0^2 + h_0^2)\, d\tau,$$

where $f_0 = f + A$, &c.,

and

$$T = \frac{\mu}{8\pi}\int (\alpha^2 + \beta^2 + \gamma^2)\, d\tau,$$

so that $\frac{1}{k\mu} = V^2$, where V is the velocity of light in the material medium considered.

These lead by the principle of least action, viz.

$$\delta\int (T - W)\, dt = 0,$$

to

$$\ddot{f}_0 = V^2\nabla^2 f_0 \quad \text{or} \quad \ddot{f} + \ddot{A} = V^2\nabla^2 f_0, \quad \&c.$$

6. But if X = the electrostatic force in the direction of x, we should have

$$X = \frac{4\pi}{k_0} f = \frac{4\pi}{k} f_0;$$

for it should have the same value, whether we regard it as arising from f or f_0.

Hence $\ddot{f} + \ddot{A} = V^2\nabla^2 f$, and two similar equations.

Finally for a plane wave, z = const., we have

$$\ddot{h} + \Sigma\ddot{C}_k = V_0^2 \frac{\partial^2 h}{\partial z^2},$$

together with

$$\ddot{C}_k + p_k^2 C_k = a_k h,$$

where C_k refers as before to the kth group of electrons.

7. These suffice for the derivation of the dispersion formula

$$n'^2 - 1 = \Sigma \frac{a_k}{p_k^2 - p'^2},$$

since we may write

$$h = h_1 e^{ip'\left(\frac{n'z}{V_0} - t\right)} \quad \text{and} \quad C = C_0 e^{ip'\left(\frac{n'z}{V_0} - t\right)}.$$

It will be observed that since $\frac{\partial A}{\partial x} = 0$ $\frac{\partial B}{\partial y} = 0$, we have $\frac{\partial C}{\partial z} = -\rho$, and therefore it will suffice to consider the equations involving C alone.

8. Now if x, y, z are the coordinates of a point referred to fixed axes, and x', y', z' those of the same point referred to axes moving with velocity $0, 0, \zeta$ uniformly, we have

$$x' = x,\ y' = y,\ z' = z - \zeta t,$$

and the transformed equations become

$$\ddot{h} + \left(\frac{\partial}{\partial t} + \zeta\frac{\partial}{\partial z}\right)^2 \Sigma C_k = V_0^2 \frac{\partial^2 h}{\partial z^2}$$

and

$$\left(\frac{\partial}{\partial t} + \zeta\frac{\partial}{\partial z}\right)^2 C_k + p_k^2 C_k = a_k h$$

(where V_0 = velocity of light in the æther),

since f, g, h being coordinates of the æther may be held to be unaffected by this motion.

9. Writing now

$$C_k = Ce^{p\left(\frac{nz}{V_0} - t\right)} \quad \text{and} \quad h = h_1 e^{ip\left(\frac{nz}{V_0} - t\right)},$$

we have

$$h_1\{(ip)^2 - (ipn)^2\} + \left(ip - \zeta i p\frac{n}{V_0}\right)^2 \Sigma C_0 = 0$$

and

$$\left(ip - \zeta ip\frac{n}{V_0}\right)^2 C_0 + C_0 p_k^2 = a_k h,$$

or

$$n^2 - 1 = \left(1 - \frac{n\zeta}{V_0}\right)^2 \Sigma \frac{a_k}{p_k^2 - p^2\left(1 - \frac{n\zeta}{V_0}\right)^2}.$$

But

$$p\left(1 - \frac{n\zeta}{V_0}\right) = p' \quad [\text{art. 11, eqn. (1)}]\ ;$$

i.e.

$$\frac{n^2 - 1}{n'^2 - 1} = 1 - 2\frac{n\zeta}{V_0}, \quad \text{nearly},$$

leaving out square terms in ζ.

10. Again, if V = velocity in the moving medium, and V' = velocity in the quiescent medium, $V - V' = \zeta\epsilon$, where ϵ is the dragging coefficient of Fresnel.

But

$$\frac{n}{V_0} = \frac{1}{V} \quad \text{and} \quad \frac{n'}{V_0} = \frac{1}{V'},$$

so that

$$\frac{n - n'}{V_0} = \frac{-\zeta\epsilon}{VV'}$$

while

$$n+n' = \frac{2V_0}{V'} \quad \text{or} \quad n^2-n'^2 = \frac{-2\zeta\epsilon V_0^2}{V'^2 V};$$

whence

$$\epsilon \frac{n'^2}{V} = (n'^2-1)\frac{n}{V_0},$$

$$\epsilon = 1-\frac{1}{n^2}, \text{ nearly.}$$

11. If, however, the motion is not to affect ρ (*i. e.* electric charge is to be an invariant, since the element of volume is unchanged on the above scheme of transformation), C should have the same value in both cases.

But if $C=C_0 e^{ip'(n'z'\sqrt{k_0}-t)}$ in a fixed medium, *i. e.* relative to the *moving* observer in a *moving* medium,

and $C=C_0 e^{ip(nz\sqrt{k_0}-t)}$ in a *moving* medium, relative to a *fixed* observer;

on identifying the two expressions (on the understanding that $z'=(z-\zeta t)$), we get

$$p'n' = pn \quad \text{and} \quad p'(1+n'\zeta\sqrt{k_0}) = p,$$

or

$$p\left(1-\frac{n\zeta}{V_0}\right) = p' \; ; \quad \ldots\ldots \quad (1)$$

but also

$$\frac{1}{n} = \frac{1}{n'}+\zeta\sqrt{k_0}. \quad \ldots\ldots \quad (2)$$

This, however, contradicts the previous result [art. 10], which, as we know, is verified by experiment.

12. This suggests that the equation of transformation should be modified. Let us write, therefore,

$$z' = \lambda(z-\zeta t) \quad \ldots\ldots \quad (1)$$

but as even this does not give the right result, we should write further

$$t' = \mu(t-\nu z) \quad \ldots\ldots \quad (2)$$

where λ, μ, ν have to be determined.

Thus $C=C_0 e^{ip'(n'z'\sqrt{k_0}-t')}$ relative to the moving observer, moving with the medium,

and $C=C_0 e^{ip(nz\sqrt{k_0}-t)}$ relative to the fixed observer.

Now comparing coefficients of z and t, on identifying the

two expressions, we have

$$p'(n'\lambda\sqrt{k_0}+\mu\nu) = pn\sqrt{k_0} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$p'(n'\lambda\zeta\sqrt{k_0}+\mu) \quad = p, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

giving

$$\frac{\frac{\lambda}{V'}+\mu\nu}{\frac{\lambda\zeta}{V'}+\mu} = \frac{1}{V} \quad \text{or} \quad V = \frac{\lambda\zeta+\mu V'}{\lambda+\mu\nu V'};$$

but $V = V' + \zeta(1 - V'^2 k_0)$ up to the first order [art. 10];

whence

$$\lambda = \mu \quad \text{and} \quad \nu = \zeta k_0 = \frac{\zeta}{V_0^2},$$

and the equations of transformation become

$$z' = \lambda(z-\zeta t), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1')$$

$$t' = \lambda(t-\zeta k_0 z). \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

13. The evaluation of λ may be effected by the use of the principle that either medium may be regarded as being in motion in relation to the other. Now, from (1′) and (2′), we get

$$\lambda z\left(1-\frac{\zeta^2}{V_0^2}\right) = z' + \zeta t',$$

$$\lambda t\left(1-\frac{\zeta^2}{V_0^2}\right) = t' + \frac{z'\zeta}{V_0^2}.$$

But on the above principle,

$$z = \lambda(z' + \zeta' t),$$

$$t = \lambda\left(t' + \frac{z'\zeta}{V_0^2}\right),$$

which gives

$$\lambda = \left(1-\frac{\zeta^2}{V_0^2}\right)^{-\frac{1}{2}}.$$

14. It is easy to verify that if λ has this value, the coefficient of ζ^2 in the period equation vanishes identically.

For, using the above transformation (1′) and (2′), the equations of motion become

$$\ddot{h}+\frac{1}{\lambda^2}\left(\frac{\partial}{\partial t}+\zeta\frac{\partial}{\partial z}\right)\Sigma C_k = V_0{}^2\frac{\partial^2 h}{\partial z^2}$$

and

$$\frac{1}{\lambda^2}\left(\frac{\partial}{\partial t}+\zeta\frac{\partial}{\partial z}\right)^2 C_k + p_k{}^2 C_k = a_k h,$$

so that we get

$$(n^2-1) = \frac{\left(1-\frac{n\zeta}{V_0}\right)^2}{\lambda^2}\Sigma\frac{a_k}{p_k{}^2-\frac{p^2}{\lambda^2}\left(1-\frac{n\zeta}{V_0}\right)^2}.$$

But $\left(1-\frac{n\zeta}{V_0}\right)\frac{1}{\lambda^2}=1-\frac{2n\zeta}{V_0}$ up to ζ^2, if $\lambda=\left(1-\frac{\zeta^2}{V_0}\right)^{-\frac{1}{2}}$.

15. The above method of deriving Lorentz transformations might appear to be less elegant than some others, such as that of Laue, but it seems to have the advantage of showing, so far as it goes, the implied dynamical mechanism. Moreover, while the method based on the principle of relativity is mainly kinematical, here we seem to get at the source of the light-signals itself.

16. In the paper above referred to, it was shown that f and f_0 may be physically interpreted as being of the nature of rotations, thus according well with various elastic solid theories of dispersion. Such a view should therefore fit in with Bohr's theory of atomic structure, but the requisite analysis will have to be held over for the present.

XLIV. *Some Cases of Polymorphic Transformation Energies.* *By* A. Hare, *M.Sc.**

Introduction.

ALTHOUGH the phenomenon of cathodo-luminescence has been the subject of careful investigations for a number of years, and a considerable amount of experimental evidence has been obtained, there has yet appeared no proved general explanation of all the facts.

Experiments † have been carried out in the Physics Laboratories of Leeds University, with the object of determining

* Communicated by Professor R. Whiddington.

† Ewles, Phil. Mag. vol. xlv. (1923).

whether the luminescence excited by cathode rays appears only when the rays acquire a minimum speed, that is, whether a definite quantum of energy is required to excite the luminescence. With each of the substances tried a definite critical velocity of the cathode rays was found. It was also found that above the temperature of transformation the cathodo-luminescence disappeared. This indicates an intimate relation between the processes involved in the molecular rearrangement and the emission of luminescence. From this the suggestion arose that luminescence is a manifestation of the energy change involved when a substance changes from one state of molecular aggregation to another.

Now, taking the minimum energy required to excite cathodo-luminescence as determined from the formula $[Ve=\frac{1}{4}mv^2]$ to represent the quantum of energy required to transform the molecular aggregate, and assuming the equipartition of this energy among the constituent molecules of the aggregate, it should be possible, from a knowledge of this energy and the molecular heat of transformation, to determine the number of molecules composing the aggregate.

The following piece of work was embarked upon in order to measure the energies of transformation of substances showing luminescent properties when bombarded with cathode rays, but, of necessity, substances not showing the above luminescent effects were in some cases used.

Previous Investigations.

A few results appear in Landolt and Börnstein's tables, but most of these have been calculated by subtracting the heats of formation of the two varieties of substance concerned. Von Hevesey * performed experiments to determine the heats of transformation of the caustic alkalies KOH, NaOH, RbOH, and CsOH. De Forcrand † investigated the case of zinc oxide, but his determination was based on an indirect chemical method, again involving heats of formation differences, and is in no way similar to the method about to be described.

Experimental Details.

The scheme involved the use of a furnace, the usual type being used. The vitreosil tube was about 70 cm. long and 5 cm. in diameter. The tube and helix were enclosed in a

* *ZS. Phys. Chem.* lxxiii. p. 683 (1910).
† *C. R.* cxxxiv. p. 1426 (1902).

thick insulating layer of magnesia with an asbestos casing round it. The whole was then placed in a large iron cylinder with terminals to which the strip was connected. A variable resistance and a choking coil were used in series with the furnace. An ampere meter was inserted in the circuit for convenience: the furnace was used in a horizontal position in order to eliminate, as far as possible, the disturbing effects of air convection currents.

In order to keep the temperature of the furnace uniform along the length of the tube, loose asbestos wool was placed in each end of the tube for a distance of about seven inches, while a square tin cap containing asbestos lagging was firmly clamped on each end of the furnace, thus completely surrounding the tube with asbestos. Thermocouples of Pt–PtRh were used. these being calibrated by taking the melting points of standard salts. A potentiometer method was used to measure the E.M.F.'s of the thermocouples, the fundamental principle of which is the adjusting of the electric circuit so that no current flows through the thermocouple. This is accomplished by balancing the E.M.F. generated in the thermocouple by an E.M.F. whose numerical value may be varied at will and measured.

Since the two E.M.F.'s are in opposition, the measurements may be made to have all the advantages of a null or zero method, which is usually desirable in precision work. The principle of the method adopted was one of comparing the heat radiated by the substance whose energy of transformation it was required to measure, with the energy radiated during the same time and under the same conditions by an equal volume of silica. Owing to the difficulty of obtaining data regarding the specific heats of substances at their transformation points it was desirable that this factor should be eliminated.

A small silica vessel was filled with a known weight of silica and fastened securely to a long twin bore rod.

Theory of the Method.

Assuming Newton's law of cooling over the small range required

$$\text{heat radiated per sec. at } P = K(\Theta - \theta),$$

where K is a constant.

$$\therefore \quad \text{total heat radiated at } P = \int K(\Theta - \theta)\, dt = mL,$$

where m = mass of salt used, and L = heat of transformation per gram.

Also from the second vessel and contents,

$$\text{heat radiated per sec.} = K(\theta' - \theta).$$

$\therefore$ total heat radiated from second vessel and contents

$$= \int K(\theta' - \theta)\, dt = \int c\, d\theta,$$

where c = thermal capacity of the second vessel and contents.

Now over the range required, $\theta' - \theta$ is a constant which we will call ϕ: also c is approximately constant for this range.

$$\therefore \qquad K = \frac{c(\theta_1 - \theta_2)}{\phi T},$$

where T = total time of transformation.

$$\therefore \qquad mL = \frac{c(\theta_1 - \theta_2)}{\phi T} \int (\Theta - \theta)\, dt.$$

Integrating this we get

$$mL = \frac{c(\theta_1 - \theta_2)}{\phi T} \left[\Theta T - \frac{\theta_\alpha^2 - \theta_\beta^2}{2} \cdot \frac{T}{\theta_1 - \theta_2} \right]$$

for

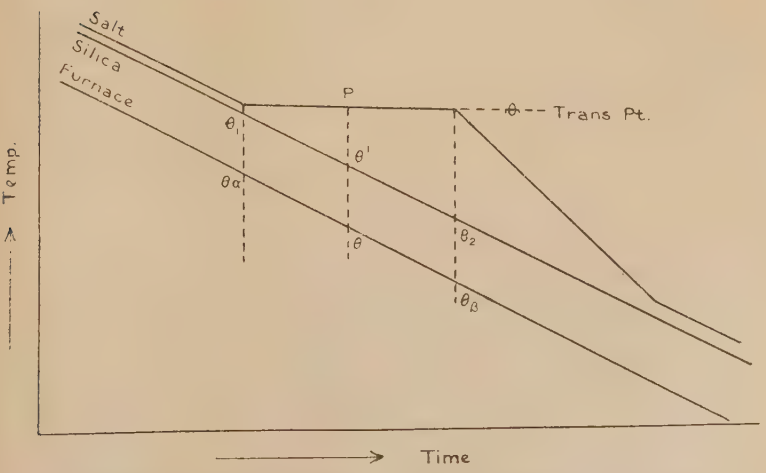
$$\frac{dt}{d\theta} = \frac{T}{\theta_1 - \theta_2}.$$

$$\therefore \qquad mL = \frac{c(\theta_1 - \theta_2)}{\phi} \left[\Theta - \frac{\theta_\alpha + \theta_\beta}{2} \right],$$

from which L, the heat of transformation, can be obtained.

These points are brought out in the curves in fig. 1.

Fig. 1.

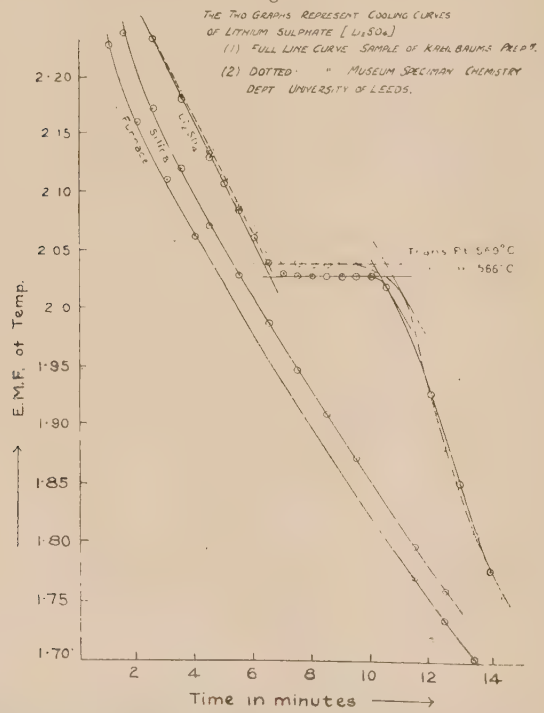


Previously it was customary to limit oneself to an estimation of the transformation point only of a salt, since the

transformation of a substance from one polymorphic state into another was considered to be a comparatively rarely appearing phenomenon.

By making use of a cooling curve an estimate of the transformation heats of various salts can be obtained. At the transformation point, the temperature remains for a time constant during the evolution of heat. Hence the transformation proceeds at a rate governed exclusively by the rate of flow of heat. If this were not the case the temperature would not remain constant for an interval, but would fall

Fig. 2.



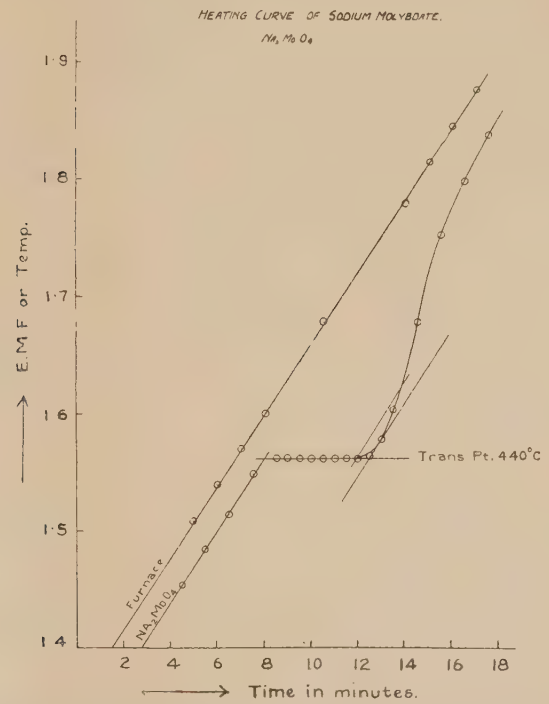
during the change with a diminished speed. With materials having extraordinarily small speeds of transformation, it appears impossible to keep the temperature of the mass constant and in such a case no horizontal part would occur on the cooling curve: merely a decrease in the rate of cooling over a certain temperature interval would be observable. In such cases the method of using cooling curves for fixing transformation points fails.

The theory just given assumes the curves to be ideal, although in actual practice the horizontal portion of the

curve is never so sharply defined, as one would naturally expect. [See figs. 2 and 3.]

The commencement of the transformation is usually well marked; the temperature then remains constant for a certain period, after which the temperature falls, slowly at first, increasing to a maximum and finally at approximately the same rate as the furnace. The end points are brought out with much greater clearness * by a method employed by Osmond in his original work on the allotropy of iron.

Fig. 3.



According to this author, the end point of the transformation occurs at the point when the temperature difference between the salt and the furnace reaches a maximum. It is also easy to show that this maximum occurs at the point when the perpendicular to the furnace curve is a maximum, or at the point where a tangent drawn parallel to the furnace curve touches the salt curve. At this point it is assumed that all the heat has been evolved. Previous to this point the heat given out by the substance causes the rate of cooling of the

* 'Dictionary of Applied Physics,' vol. v. p. 438

salt to be less than that of the furnace, while after this point, when all the heat has been evolved, the temperature of the substance falls much more rapidly until, once again, the constant difference in temperature is reached.

At the critical point, the rate of cooling is along the tangent at that point. The heat of transformation can then be calculated from the formula previously mentioned.

Results.

In order to test the method it has been applied to a redetermination of the known latent heats of substances at high temperatures. The substances chosen were common salt and potassium chloride. The results given for these two substances by the method described agree with those of Plato *, different weights of the substance being taken in both cases.

The photographic reproduction (fig. 2) of the original graphs for lithium sulphate shows the type of curves.

In this case two samples were taken: (1) prepared by Messrs. Kahlbaum, Berlin, and (2) a museum specimen supplied by the Chemistry Department of the University. The following table shows the results for the substances experimented upon.

Substance.	Melting point in °C.	Latent heat in kg. cal. per gram mol.
Common salt	800	1. 7·22
		2. 7·14
Potassium chloride.....	772	1. 6·32
		2. 6·29

Substance.	Trans. point in °C.	Heat of trans. in kg. cal. per gram. mol.
Potassium sulphate.....	569	2·57
Potassium chromate	664	2·45
Lead sulphate	866	4·06
Lithium sulphate (1)	566	6·77
(2)	569	6·96
Sodium molybdate	440	14·60
Sodium tungstate	579	9·51

In the case of every substance tried, with the exception of sodium molybdate, the heat of transformation could be obtained equally well from either a cooling or a heating curve. This, in effect, means that for these substances the transformation is immediately reversible. In the case of sodium molybdate, however, a time effect was observed.

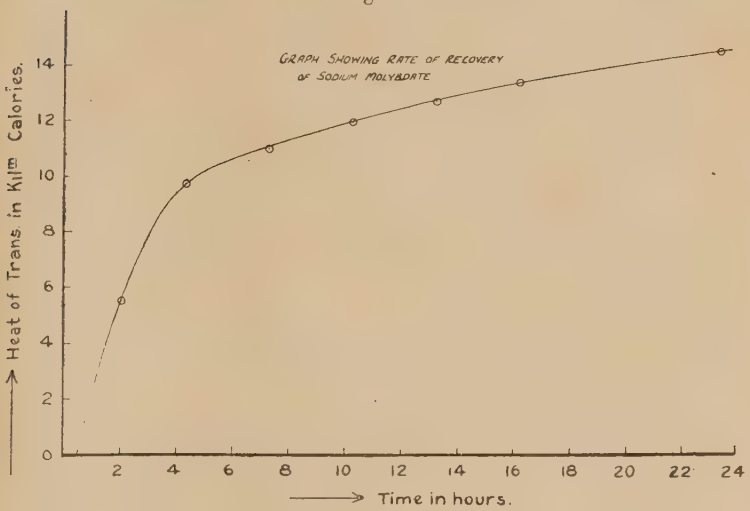
This means that while the transformation could be measured from a heating curve, no effect was observed on

* Plato, *ZS. Phys. Chem.* 1906.

immediately cooling. This indicates that the transformation does not reverse immediately, but either after a certain interval of time or not at all. Experiments were carried out in order to investigate this point further.

The diagram (fig. 3) shows the curve obtained on heating sodium molybdate, and, as will be seen, is similar in all respects to the cooling curves shown in the case of lithium sulphate. A quantity of sodium molybdate was heated up slightly above the transformation temperatures. When it had all transformed it was taken out of the furnace and kept at room temperature, approximately 20° C. Readings were taken on the substance at intervals of three hours for a period of about twenty-four hours. The readings enabled a curve to be drawn showing the rate of recovery of the substance to its original state after having first been transformed by heating. A reproduction of this curve is given in fig. 4.

Fig. 4.



Interpretation of Results obtained with Sodium Molybdate.

1. Exponential method.
2. Explanation bearing on a formula, due to Steinmetz, for the characteristic curve of iron.

Exponential Method.

The ordinates of the curve (fig. 4) represent the heat of transformation in kilogram calories per gram molecule, while the

abscissæ represent the time in hours. It will be observed that when $T=0$ the amount of substance recovered equals zero, while when $T=\infty$ the substance has totally recovered.

The ordinates will be represented by M and the abscissæ by T in the following part of the paper.

$\therefore$ when $T=0$, $M=0$;

and when $T=\infty$, $M=M\infty$,

where $M\infty$ = total heat of transformation.

Instead of using the actual curve obtained, a curve was drawn showing the relation between the amount of substance still to be transformed and the time.

Thus when $T=0$, $M=0$ and $M\infty - M = M\infty$;

and when $T=\infty$, $M=M\infty$ and $M\infty - M\infty = 0$.

It was then attempted to resolve this curve into a series of exponential terms, the number of terms being limited to two or three.

Two or three exponential terms, however, do not fit such a curve with any great degree of accuracy.

Explanation bearing on Characteristic Curve of Iron.

During the work on the curve satisfying the conditions that when $T=0$, $M=0$ and when $T=\infty$, $M=M\infty$, it was noticed that on plotting $\frac{T}{M}$ against T a straight line was obtained.

This suggests a formula

$$\frac{T}{M} = a + bT,$$

where a and b are constants.

The constants can be calculated by the method of least squares, giving

$$\frac{T}{M} = 0{\cdot}255 + 0{\cdot}0596\,T.$$

Returning to the equation $\frac{T}{M} = a + bT$ or $M = \frac{T}{a+bT}$, a further constant M_0 is needed to make the equation dimensionally correct. Then $M = M_0 \cdot \frac{T}{a+bT}$.

Differentiating this with respect to time we get

$$\frac{dM}{dt} = \left(\frac{a}{M_0}\right)\left(\frac{M}{T}\right)^2 \quad \ldots\ldots \quad (1)$$

where a and M_0 are constants.

Now, eliminating T from the right hand side of the equation,

$$\frac{dM}{dt} = M^2 \cdot \frac{b^2}{M_0 a} - 2M\frac{b}{a} + \frac{M_0}{a}.$$

This can be split into

$$\frac{dM}{dt} = (M-\alpha)(M-\beta),$$

where α and β are constants.

This is consistent with the view that two monomolecular changes are proceeding at the same time.

It is interesting to note that the equation $\frac{T}{M} = a + bT$ also fits the characteristic curve in the case of iron.

The phenomenon of magnetization is known to be a breaking up of the molecular aggregates with a definite lagging effect after the force has been removed and appears, therefore, to be a similar problem.

In conclusion, I wish to thank Professor Whiddington for suggesting the problem and for his generous and kindly advice during the carrying out of the work.

The Physics Laboratories,
The University, Leeds.
10th June, 1924.

XLV. *On an Active Modification of Nitrogen.* *By* M. N. Saha *and* N. K. Sur, *Allahabad University, Allahabad, India* *.

A FEW years ago Prof. Strutt (now Lord Rayleigh) performed a series of experiments on an active modification of nitrogen †, which excited a good deal of interest at the time. Nitrogen is well known to be an extremely inert gas, but Lord Rayleigh showed that if a condensed spark discharge be sent through N_2-gas, the glow persists in the gas flowing out of the region of the discharge, which shows considerable chemical and spectral activities. The spectrum of the afterglow was investigated by Fowler and Strutt ‡

* Communicated by the Authors.

† Strutt, Proc. Roy. Soc. Lond. lxxxv. p. 219; lxxxvi. pp. 56, 105, 262, 529; lxxxvii. pp. 179, 302, 381; lxxxviii. pp. 110, 539.

‡ Fowler and Strutt, Proc. Roy. Soc. Lond. lxxxvi. pp. 105–117.

and shown to consist of the usual α, β, and γ groups of positive bands, with a fourth group which was observed for the first time.

The object of the present paper is to show that almost the whole series of observations recorded by Lord Rayleigh can be explained on the basis of Klein and Rosseland's theory * of inelastic collision of the second type, which has been further developed by Franck † and his students. For convenience of discussion we begin with a short account of this theory.

The experiments on ionization potential and origin of spectra, which were first carried out by Franck, are now matters of common knowledge. They deal with the interchange of energy between freely moving electrons and atoms. A stream of electrons moving with a definite velocity is projected into a mass of gaseous atoms. When an electron happens to pass close to an atom, then, provided the energy of the free electron exceeds a certain limit given by the quantum condition $eV = h\nu$, the whole of its energy may be transferred to the valency electrons lying at the outer periphery of the atom. The valency electron is thereby lifted to higher quantum orbits. These states are not stable, and in a short time it reverts to its original position, the excess of energy being set free as monochromatic radiation. Thus the atoms abstract energy from the free electrons, and convert it to energy of its own monochromatic radiation. This process is indicated by kicks in the current-potential curves, as well as by the emission of the characteristic spectrum of the element. When the energy of the bombarding electron is sufficiently large, it may tear off the valency electron from the parent atom. This stage is known as ionization and indicated by an abrupt rise of the current in the current-potential curve.

Hitherto, attention of all workers has been confined to only one side of the problem, *i. e.*, communication of energy by the free electron to the atom. But Klein and Rosseland showed that the reverse process (viz., communication of energy by the excited atom to the free electron) actually takes place in nature on a very large scale, and accounts for a large number of experimental results recorded in previous years. For example, suppose we have a mass of mercury atoms, some of which has been activated either by absorption

* Klein and Rosseland, *Zs. f. Physik*, iv. p. 46.

† Franck, *Zs. f. Physik*, ix. p. 259; xi. p. 155. Cario, *Zs. f. Physik*, x. p. 105 and p. 166. Compton, Journal of the Optical Society of America, 1923.

of the light $\lambda=2536$ ($1S-2p_2$) or by an electric discharge from the normal ($1S$) stage to the next stage $2p_2$. If, now, an electron passes close to this mercury atom ($2p_2$ stage), what will take place? According to older conceptions, we could think of no other process than that the electron would communicate its energy to the mercury atom, and excite it to still higher quantum states or to ionization. But Klein and Rosseland pointed out that the reverse process may also take place, viz., the mercury atom may transfer its extra amount of energy corresponding to $\lambda=2536$ to the electron. The electron thus receives an increment in its velocity, but the transfer is "*radiationless*," *i. e.* the electron *chokes the emission* of the light $\lambda=2536$, which would have otherwise certainly taken place. The chance of this "radiationless transfer" depends upon circumstances which are yet to be worked out, but there seems to be no doubt that it is a very general phenomenon *.

These considerations were further extended by Franck and his students, who showed that the excited atoms may communicate their energy not only to the electron, but also to such atoms or molecules as may come in contact with them. These atoms or molecules will therefore receive either some increment in their kinetic energy or, if the energy imparted be sufficiently large, they may be excited to their spectral emission, ionization or dissociation in the case of molecules.

These ideas, therefore, open up a very promising field of investigation, and Franck has already pointed out, and confirmed several interesting deductions. For example, a stream of mercury gas was excited by $\lambda=2536$, and these activated Hg atoms were allowed to act upon the H_2-gas. It was proved that the H_2-gas was thereby dissociated into atoms. The explanation is that when a mercury atom absorbs the light $\lambda=2536$, it is loaded to an energy-content of 4·9 volts. On coming into contact with the H_2-gas it

* It may be noted here that Klein and Rosseland were led to this conception from Einstein's idea of "Negative Einstrahlung" or negative absorption. A Hertzian oscillator when placed in a field of radiation may either take up the energy from the field, or give up its own energy to the field, according as the phase difference between the vibration of the resonator and the incident radiant waves is less or greater than 90°. The former case is positive absorption, energy being taken up by the resonator from the field. The latter case is negative absorption, energy being given to the field, just as in alternate current instruments, if the phase difference between the current and potential is $>90°$, the work done by the instrument $EI\cos\phi$ becomes negative, *i. e.*, work has to be done on the instrument.

delivers this energy to the molecule of H_2, which is thereby broken up into atoms, as the heat of dissociation corresponds to about 3·8 volts (80000–90000 cal.).

Transference of energy to atoms.

Hg atoms activated by $\lambda = 2536$ were allowed to act upon vapours of thallium and silver. Only such lines of these vapours were excited for which the energy required is less than 4·9 volts.

Choking Effect of Inert Gases on Luminous Mercury Vapour.

Wood * carried out years ago a number of very interesting experiments on the luminescence of mercury vapour excited by an electric discharge. He found that if inert gases like N_2, He_2, A were added to the luminous Hg-vapour, the luminosity was quenched, the decrease in luminosity being roughly proportional to the amount of gas added. The explanation according to Franck is as follows:—When an activated Hg atom comes into collision with an atom of A or He, then in some cases energy is communicated to the latter. This results simply in an increase of the kinetic energy of the A or the He atom, as the amount of energy transformed (4·9 volts) is quite insufficient to lift the vibrating electron of A or He to the higher orbit. The net result is, therefore, the quenching of the line $\lambda = 2536$ A.U. or other lines of the Hg spectrum.

The phenomenon is therefore quite general. If to a mass of luminous gas another gas is added of which the radiation potential is higher than that of the luminous gas, the luminosity is choked.

To those who have followed the work of Lord Rayleigh on active nitrogen, the foregoing discussion would seem to hold out promises of a very satisfactory explanation. But all is not plane sailing as the following discussion will show. We begin with a concise statement of our explanation.

When a moderately condensed discharge is sent through N_2-vapour it is converted into an excited state, falling just short of dissociation into its constituent atoms. The amount of energy to which the molecule is loaded lies between 8·2 and 8·5 volts. The average life of such an excited atom is of the order of 10^{-3} second. When the excited nitrogen

* Wood, *Phys. Zs.* xiii. p. 353 (1912).

molecule falls back to the original state, it emits a band-spectrum lying between $\lambda=1600$ and $\lambda=1200$*.

This band may be called the primary band, and the usual bands lying in the visible region (the positive bands) stand to this in the same relation as the subordinate series of an element stand to the lines of the principal series.

The arguments in favour of this view are as follows :— The spectrum of active nitrogen was investigated by Fowler and Strutt †, and found to consist of the α and β groups of positive bands, which according to the canal-ray method of Wien ‡ are due to the N_2 molecule. None of the lines of the familiar line-spectrum (attributed by Fowler to N^+) were observed. (It is still a moot point whether the lines due to N atom, recorded by Stark and Hardtke §, were present, as the above-mentioned investigations did not extend up to this region.) None of the negative bands, which according to Wien are due to N_2^+, were present.

The evidence is thus fairly conclusive that N_2-gas in the afterglow region simply consists of excited N_2 molecules. The experiments of Lord Rayleigh ‖ to detect whether charged particles were present in the afterglow were entirely negative.

It is also clear that the afterglow bands cannot be the primary bands, for unexcited N_2-gas is completely transparent to this region. It has got an absorption band lying between $\lambda=1600$ Å.U. and $\lambda=1200$ Å.U. That the primary band lies in this region is also proved by the experiments of Brandt ¶, who, using the bombarding electron method of Franck, found an abrupt rise of current in the neighbourhood of 8·2 volts. Several kicks were observed in the current-potential curve between 8 and 9 volts, and these were shown by Brandt to be of the nature of band-emission. The primary emission bands therefore lie between $\lambda=1600$ and $\lambda=1200$ Å.U., and are present in the afterglow region. But the glass of the quartz vessels in which these experiments are carried out completely masks them.

The visible bands which are actually observed are simply secondary. Their final orbit is also unstable, just as the final orbits corresponding to the Balmer-lines of H are the

* Lyman, 'The Spectroscopy of the Ultra-Violet,' p. 63.
† Proc. Roy. Soc. Lond. lxxxvi. pp. 105–117.
‡ Wien, *Ann. d. Physik*, lxix.
§ Stark and Hardtke, *Ann. d. Physik*, lvi. p. 303.
‖ Strutt, Proc. Roy. Soc. Lond. lxxxviii. p. 183.
¶ Brandt, *Zs. f. Physik*, viii. p. 32.

diquantic unstable orbits. These bands will therefore be emitted only when these orbits have a certain amount of stability.

According to this view, active nitrogen simply consists of the excited nitrogen molecule loaded to the energy of about 8·5 volts (corresponding to about $1{\cdot}9 \times 10^5$ calories). Its great activity is due to the ease with which the particle can part with this amount of energy. When foreign atoms or molecules are not present or present only in small amounts, the excited molecule reverts to the normal state after emission of the primary and the secondary (the usual positive) bands. The average life of the excited atom when it suffers no collision is about 10^{-8} sec. *, but this may be lengthened when the number of collisions is large. This point will be discussed later on.

When foreign substances are present, the energy is mostly communicated in a radiationless transfer. The foreign substance is thereby stimulated either to luminescence or to chemical activity. The following few selected examples will bring out the point clearly.

(1) Active nitrogen, when passed over sodium, causes not only the D_1 and the D_2 lines, but also the subordinate series lines to flash out.

The amount of energy required for the excitation of the yellow lines is only 2·1 volts, so that the energy delivered by active nitrogen is sufficient, not only for exciting its entire line-spectrum, *but may probably also suffice to ionize it*, as well as the other alkali elements. Lord Rayleigh found that the maximum emission is at the second line of the principal series 3303. This is probably due to the fact that the energy transferred is very large compared with the excitation potential of Na.

* Wien's method of determining the charge on luminous atoms may be noted here. He allowed a stream of luminous gas to flow out of a canal-ray tube into a space where a vacuum of the order of 10^{-3} to 10^{-4} mm. is continuously maintained by a number of diffusion pumps. In this space, the gas is allowed to pass between two parallel plates which are maintained at a small distance apart at a constant difference of potential. The spectrum of the luminous slit-like region is photographed. Particles which are uncharged show straight spectral lines, while lines due to charged particles are bent one way or the other. The vacuum in the space is so high that no collision takes place amongst the particles. In this way Wien proved that the β groups of positive bands are due to the uncharged N_2 molecules, whereas the bands in the negative glow are due to N_2^+ molecules.

(2) Action on mercury.

Active nitrogen, passed over Hg-vapour, excites the fundamental line $\lambda=2536$ ($1S-2p_2$) and lines belonging to the triplet group of the first subordinate and second subordinate series. The 2P–3D line ($\lambda=5790$) and $2P-3d_2'$ line ($\lambda=5769$) are not excited, hence probably an upper limit to the energy transferred is obtained by assuming that it just fails to excite the 3D level in the Hg-atom. This is 9·4 volts, which is in accordance with our theory.

(3) Action on magnesium.

Many arc-lines are developed, but neither the line 4481 nor any other spark-line was excited. The arc-line $\lambda=4703$ (1P–4D) was either not excited at all or excited very feebly.

The ionization potential of magnesium is 7·65 volts, and thus active nitrogen would just suffice to ionize magnesium. Active nitrogen passed over Ca, Ba, or Sr, would excite, besides their arc spectrum, also the spark spectrum.

(4) Hydrogen and the inert gases have no other influence on active nitrogen except a mere dilution of the glow. This is in accordance with the fact that the minimum excitation potential of these gases is much higher than the maximum energy which can be transferred by active energy.

On the other hand, when helium is activated by an electric discharge, it is capable of storing a large amount of energy ($e=20·4$ volts) and hence would be found to be an extremely active substance. This view is supported by an interesting observation of Lord Rayleigh * in a recent paper, who found that activated helium on coming into contact with N_2-gas (unexcited) excites the afterglow. If the present view is correct, it would excite not only the positive bands but also the line-spectrum due to N. This point ought to be further investigated.

We now come to the most formidable difficulty confronting the above explanation, viz., chemically pure nitrogen shows no afterglow at all. This matter forms the subject matter of a very interesting paper by Lord Rayleigh in vol. xci. of the P. R. S. London. Following experiments by Tiede and Domcke, who found that chemically pure nitrogen, prepared by heating barium and potassium azide, and carefully freed from all impurities, shows no afterglow at all, Lord Rayleigh showed that nitrogen purified by prolonged standing over

* Lord Rayleigh, Proc. Roy. Soc. Lond. vol. cii. p. 454.

the liquid alloy of Na and K gave an afterglow, which was however very faint. On introducing small impurities of oxygen, or almost any easily excitable gas (1 in 1000 parts), the glow was restored to full brilliancy. This observation has also been confirmed by recent experiments of Pirani *, who claims for his nitrogen a purity of 5×10^{-5} per cent. Pirani finds that perfectly pure N_2 shows no luminescence at all, though admixture of electronegative gases like O_2, H_2O, I_2 in concentration of $1{\cdot}5 \times 10^{-3}$ give a maximum after-luminescence. Large admixtures, say from 6 to 8×10^{-3}, choke the luminescence. In all these experiments, the authors seemed to have looked only for the after-luminescence of the chemically pure gas as a test of activity. They did not evidently apply the chemical tests. This point is of some importance, because the afterglow is simply the sign of the return of the molecule from the higher quantum states to one of the intermediate unstable states; it does not indicate the reversion to the normal state. Hence, if under certain conditions the intermediate orbits (*i. e.* final orbits of the afterglow band) be not stable, these will not be emitted at all, though the gas will exhibit all the chemical and spectral activity recorded by Lord Rayleigh.

It seems to be a general phenomenon that the activated atom, when left to itself, has always a tendency to fall to the lowest quantum state, without stopping at the intermediate stages. Hence only the primary bands would be emitted. This is confirmed by an interesting investigation of Wood †, who finds that in his discharge-tubes, Balmer lines of H (for which the final orbit is an unstable orbit) are always rendered very brilliant if H_2O vapour is present as an impurity. The subject is, however, well worth further investigation.

Our explanation of the absence of afterglow in active nitrogen, if true, would mean that nitrogen may be loaded to an energy of about 8·5 volts without being luminous, and therefore will still possess all other properties associated with active nitrogen.

* Pirani, 'Chemical Abstracts,' 1923, ii. p. 157.
† Wood, Phil. Mag. xlii. p. 729.

XLVI. *Faraday's "Magnetic Lines" as Quanta.*—Part II.

By Prof. H. Stanley Allen, *M.A.*, *D.Sc.* *

Introduction.

PART I. of the paper bearing the above title was published in the Philosophical Magazine for October 1921. At the Edinburgh meeting of the British Association in that year, I gave an account of the principal results of the paper and exhibited the mechanical model to be described in the present communication. At the same meeting Prof. E. T. Whittaker discussed electromagnetic tubes of force in four dimensions, pointing out that the ordinary electrostatic and magnetic tubes were dependent on the relative state of rest or motion of the observer. These results, which were subsequently developed in an important paper read before the Royal Society of Edinburgh †, led me to withold from publication the material already prepared for Part II. of my own paper. It appeared to me, as I suggested at the time ‡, that it might be necessary to regard the four-dimensional tubes, or "calamoids," of Prof. Whittaker as the true units required by the quantum theory. This view was strengthened in conversation and correspondence with Prof. Whittaker. Further consideration, however, has inclined me to believe that, even though there may be advantages in regarding calamoids as Quanta, there is still something to be learnt from the more familiar magnetic tubes in three dimensions. Two factors have influenced me in coming to this conclusion. In the first place, Prof. Whitehead, whose authority on the philosophical aspects of relativity is undoubted, has stated recently § :— "The aim of the Einstein theory is to derive physical laws of such a general character as to be independent of the peculiarities imposed on measurements by the particular circumstances in which they are made. But this is an arbitrary demand : it may well be that those peculiarities are expressions of the essential realities underlying the phenomena." In the second place, Leigh Page ‖ in an interesting paper has distinguished between "intrinsic magnetic fields," which cannot be annihilated by the

* Communicated by the Author.
† Proc. Roy. Soc. Edin. xlii. p. 1 (1921).
‡ 'Nature,' cviii. p. 341 (1921).
§ Proc. Phys. Soc. Lond. xxxvi. p. 193 (1924).
‖ Phys. Rev. xxii, p. 188 (1923).

Lorentz transformation, and fields which depend on the observer's state of rest or motion.

In his Report on "The Quantum Theory" (1923)* Prof. E. P. Adams has devoted a chapter to a discussion of the possibility of a magnetic interpretation of the theory. This contains a useful summary of the work done and of the present position of the problem.

It was shown in Part I. that when a charge e is moving in an orbit of any shape whatever with high frequency ν, there is, associated with each canonical coordinate a magnetic flux of an integral number of quantum tubes, the unit tube being defined by the ratio h/e, where h is Planck's constant. There is a magnetic flux through the orbit which may be considered as constituted by a definite whole number of discrete magnetic tubes defined as above. It is of interest to see whether the ideas suggested by the simple cases already dealt with can be applied to more complex distributions. This question is discussed in the first half of the present paper.

In § 1 and § 2 I reproduce the work on quantum magnetic tubes for two current circuits, substantially as it was written in 1921, although I recognize that the method of applying the quantum conditions is open to serious criticism. The results obtained are, however, justified by the more rigorous treatment given in § 3, for which I am indebted to Prof. C. G. Darwin. The extension to any number of current circuits is discussed in the following section. The second half of the paper is concerned with a somewhat speculative attempt to apply the results obtained to Bohr's theory of spectral series.

1. Quantum Tubes for two Current Circuits.

We consider as a typical case of a more complex distribution two current circuits, which may be thought of as representing either two magnetons or two electron orbits. The electrokinetic energy is given by the well-known expression

$$\tfrac{1}{2}\mathrm{L}_1 i_1^2 + \tfrac{1}{2}\mathrm{L}_2 i_2^2 + \mathrm{M}_{12} i_1 i_2, \quad . \quad . \quad . \quad . \quad (1.1)$$

where i_1 = current in the first circuit,
i_2 = current in the second circuit,
L_1 = self-inductance of the first circuit,
L_2 = self-inductance of the second circuit.
M_{12} = mutual inductance of the two circuits.

* Bulletin of the National Research Council, No. 39, Washington.

This may be re-written in the form

$$\tfrac{1}{2}(L_1-M_{12})i_1^2+\tfrac{1}{2}(L_2-M_{12})i_2^2+\tfrac{1}{2}M_{12}(i_1+i_2)^2, \quad (1.2)$$

to which it is proposed to apply the quantum conditions.

The quantum theory requires that, when the kinetic energy of a system is expressed in the form

$$\tfrac{1}{2}A_1\dot{q}_1^2+\tfrac{1}{2}A_2\dot{q}_2^2+\ldots \equiv T_1+T_2+\ldots \quad . \quad . \quad . \quad . \quad . \quad (1.3)$$

(q_1, q_2, . . . being Hamiltonian positional coordinates), the discontinuous energy exchanges always occur in such a way that the steady motions satisfy the equations

$$\left.\begin{aligned} 2\int T_1\,dt &= n_1h,\\ 2\int T_2\,dt &= n_2h,\\ &\ldots\ldots \end{aligned}\right\} (n_1, n_2, \ldots \text{integers}), \quad . \quad (1.4)$$

the integration in each case being extended over the corresponding period.

It must be observed that the expression (1.2) for the electrokinetic energy differs from (1.3) in the fact that the third term contains the square of i_1+i_2, a quantity which depends on the variables i_1 and i_2 involved in the first two terms. Consequently, we are not strictly entitled to use the quantum conditions (1.4).

These conditions were first stated by W. Wilson *, and are equivalent to those used by Sommerfeld † in discussing the fine structure of spectral lines.

With the above reservation the quantum conditions in the present case may be written

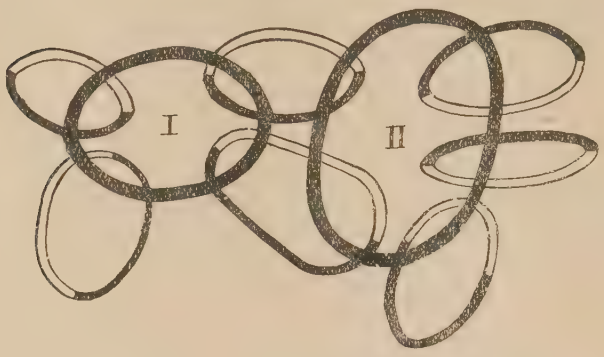
$$\left.\begin{aligned} \int(L_1-M_{12})i_1^2dt &= n_1h\\ \int(L_2-M_{12})i_2^2dt &= n_2h\\ \int M_{12}(i_1+i_2)^2dt &= n_{12}h \end{aligned}\right\} (n_1, n_2, n_{12} \text{ integers}) \quad . \quad (1.5)$$

Now, defining magnetic tubes in the way customary in electromagnetic theory, L_1i_1 is the number of magnetic tubes passing through circuit 1 due to its own current, and $M_{12}i_1$ is the number of tubes passing through circuit 2 due to the current in circuit 1. The difference between these

* W. Wilson, Phil. Mag. xxix. p. 795 (1915); xxxi. p. 156 (1916).
† Sommerfeld, *Ann. d. Physik*, li. p. 194 (1916).

gives the number of tubes that are linked *only* with circuit 1 (see fig. 1).

Fig. 1.



Magnetic tubes associated with two current circuits.

The two current circuits I. and II. are shown in black. In this case
N_1, the number of tubes linked only with circuit I. is 2,
N_2, the number of tubes linked only with circuit II. is 3,
N_{12}, the number of tubes linked with both circuits is 2,
$\mathcal{N}_1$, the total number of tubes linked with circuit I. is 4,
$\mathcal{N}_2$, the total number of tubes linked with circuit II. is 5,
whilst the total number of tubes in the diagram is 7.

Thus $L_1 i_1 - M_{12} i_1 = N_1 =$ number of tubes linked *only* with circuit 1. . . (1.6)

Again $L_2 i_2 - M_{12} i_2 = N_2 =$ number of tubes linked *only* with circuit 2. . . (1.7)

And $M_{12}(i_1 + i_2) = N_{12} =$ number of tubes linked with both circuits . . . (1.8)

It may be remarked that the *total* number of tubes is

$$L_1 i_1 + L_2 i_2 = N_1 + N_2 + N_{12}. \quad . \quad . \quad . \quad (1.9)$$

Also the total number of tubes linked with circuit 1 is $L_1 i_1 + M_{12} i_2 = \mathcal{N}_1$, and the total number of tubes linked with circuit 2 is $M_{12} i_1 + L_2 i_2 = \mathcal{N}_2$, results which will be required later.

With this notation the quantum conditions become

$$\left.\begin{aligned} N_1 \int i_1 \, dt &= n_1 h \\ N_2 \int i_2 \, dt &= n_2 h \\ N_{12} \int (i_1 + i_2) \, dt &= n_{12} h \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1.10)$$

Now, $\int i_1\,dt$ integrated over a complete period represents the total quantity of electricity passing round the circuit, and, according to the electron theory, this must be an integral number of times the electron charge, or $=k_1e$, where k_1 is an integer.

In this way we obtain the results

$$\left.\begin{aligned} k_1\mathrm{N}_1e &= n_1h \\ k_2\mathrm{N}_2e &= n_2h \\ k_{12}\mathrm{N}_{12}e &= n_{12}h \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (1.11)$$

where k_1, k_2, k_{12} are integers.

The only difficulty which presents itself here is with regard to the limits to be assigned to the integration in $\int (i_1+i_2)\,dt$. This question may be elucidated by means of a mechanical analogy to be considered in the following section.

The quantum conditions may be written

$$\left.\begin{aligned} \mathrm{N}_1 &= \frac{n_1}{k_1}\left(\frac{h}{e}\right) \\ \mathrm{N}_2 &= \frac{n_2}{k_2}\left(\frac{h}{e}\right) \\ \mathrm{N}_{12} &= \frac{n_{12}}{k_{12}}\left(\frac{h}{e}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1.12)$$

The simplest interpretation of these results is to assume the existence of discrete quantum tubes of magnetic induction determined by the ratio h/e. In Bohr's later theory of atomic structure the several electrons of the complex atom, instead of forming rings as in the earlier model, are supposed to be moving each in its own independent orbit. Thus, in general, in an atomic or molecular system, k_1, k_2, and k_{12} will be unity. Even were this not so in a particular case, the value of n might be supposed an integral multiple of the corresponding k *.

2. A Mechanical Model for two Current Circuits.

In a letter dated Christmas 1876, Clerk Maxwell † wrote: "I have been making a mechanical model of an induction

* The possibility of the existence of "half-quanta," which have been assumed by several investigators within recent years, may be bound up with the occurrence of the fractions n/k.

† Campbell and Garnett, 'Life of James Clerk Maxwell,' pp. 396-551 (1882).

coil, in which the primary and secondary currents are represented by the motion of wheels, and in which I can symbolize all the effects of putting in more or less of the iron core, or more or less resistance and Leyden jars in either circuit."

This model, of which a copy is preserved in the Cavendish Laboratory, Cambridge, and another in the George III. Museum of King's College, London, is described and illustrated in Maxwell's biography and in Webster's 'Electricity and Magnetism' (p. 140) *. The essential part of the mechanism is a differential train of wheels, such as is often employed as a dynamometer and is now familiar in connexion with a motor car. The primary and secondary circuits are represented by two circular disks mounted so as to turn independently about horizontal axes in the same straight line. On the shaft of each disk is mounted a bevel wheel, A and B in fig. 2, and these gear into a third bevel wheel D, which turns loosely on a shaft at right angles to the former pair. This shaft itself, which carries a system composed of four projecting arms of adjustable moment of inertia, can rotate about the same horizontal line as the two disks. A and B can turn independently of each other, except in so far as they are connected through D. Thus the two disks are in mechanical connexion exactly as the driving wheels of a motor car are connected through the differential gearing.

The resemblance between the mechanical and the electrical systems is best seen by writing down expressions for the kinetic energy. Let I_1, I_2 be the moments of inertia for the disks, I_{12} the moment of inertia for the central system. Let ω_1, ω_2, ω_{12} be the corresponding angular velocities. The kinetic energy of the mechanical system is

$$\tfrac{1}{2}I_1\omega_1^2+\tfrac{1}{2}I_2\omega_2^2+\tfrac{1}{2}I_{12}\omega_{12}^2. \quad . \quad . \quad . \quad . \quad (2.1)$$

In the actual model the bevel wheels are all alike, and the angular velocity of the central part is the mean of the angular velocities of the disks, or $\omega_{12}=\tfrac{1}{2}(\omega_1+\omega_2)$. In this case the kinetic energy can be written in the form

$$\tfrac{1}{2}I_1\omega_1^2+\tfrac{1}{2}I_2\omega_2^2+\tfrac{1}{2}\frac{I_{12}}{4}(\omega_1+\omega_2)^2. \quad . \quad . \quad . \quad (2.2)$$

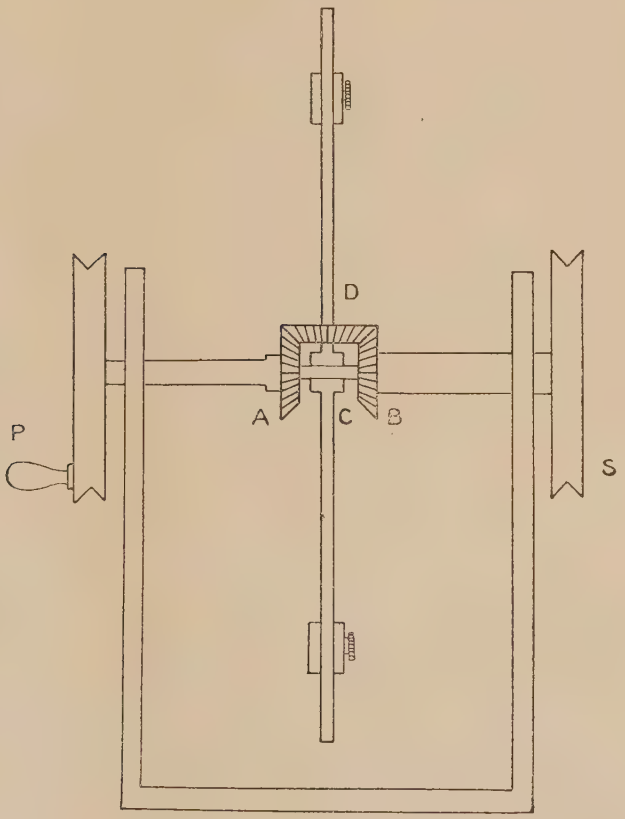
* The same mechanical analogy has been applied to coupled oscillating circuits by Pomey, *Rev. Gén. d'El.* i. p. 83, Jan. 1917; p. 163, Feb. 1917.

Comparing this with the expression,

$$\tfrac{1}{2}(L_1-M_{12})i_1^2+\tfrac{1}{2}(L_2-M_{12})i_2^2+\tfrac{1}{2}M_{12}(i_1+i_2)^2, \quad (1.2)$$

for the electrokinetic energy of two current circuits, we see that the currents are represented in the model by angular velocities, the inductances by moments of inertia.

Fig. 2.

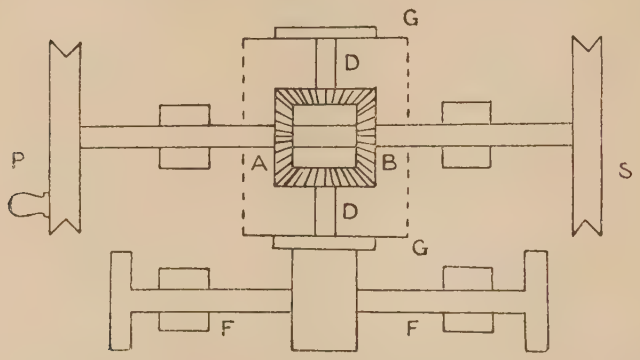


With the object of producing a closer correspondence between the electrical and the mechanical systems, I have devised a modification of Maxwell's mechanism. In this modified apparatus there are three shafts A, B, and F, so connected that the angular velocity of the third shaft F is the algebraic sum of the angular velocities of the independent side shafts A and B, giving

$$\omega_{12}=\omega_1+\omega_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

The shaft which carries the bevel wheels DD is attached to the gear-case, and these all rotate with angular velocity $\frac{1}{2}(\omega_1+\omega_2)$. To effect the desired result it is only necessary to make the gear-case drive the shaft F at double its own speed. This may be done by a belt or chain drive, or by means of pinion wheels as in the model shown in fig. 3.

Fig. 3.



The kinetic energy of the modified mechanism * is given by

$$\begin{aligned}&\tfrac{1}{2}I_1\omega_1^2+\tfrac{1}{2}I_2\omega_2^2+\tfrac{1}{2}I_{12}\omega_{12}^2\\&=\tfrac{1}{2}I_1\omega_1^2+\tfrac{1}{2}I_2\omega_2^2+\tfrac{1}{2}I_{12}(\omega_1+\omega_2)^2. \quad . \quad . \quad (2.4)\end{aligned}$$

This expression is exactly analogous to

$$\tfrac{1}{2}(L_1-M_{12})i_1^2+\tfrac{1}{2}(L_2-M_{12})i_2^2+\tfrac{1}{2}M_{12}(i_1+i_2)^2, \quad (1.2)$$

which represents the electrokinetic energy of two current circuits. The currents are still represented in the mechanical system by angular velocities, the inductances by moments of inertia, but in this model the mutual inductance corresponds directly to the moment of inertia of the third shaft. The angular momenta of the three parts of the mechanism correspond to the number of magnetic tubes linked with the primary circuit, the secondary circuit, and the two circuits, respectively. The resemblance between the mechanical model and the current circuits in this latter respect is of special interest, seeing that according to Nicholson's quantum hypothesis angular momentum can be expressed as an integral number of times the unit $h/2\pi$, whilst according to the present suggestion the magnetic tubes are multiples of a discrete quantum tube defined by h/e.

* The amount of inertia of the gear-case is supposed negligibly small in comparison with that of a shaft.

Returning now to the quantum conditions in (1.10), let us suppose that in finding the value of the integral $\int (i_1+i_2)\,dt$ in the steady state, the integration is extended over the complete period, $1/\nu_{12}$, corresponding to the time of revolution of the third shaft of the modified mechanism with angular velocity $\omega_{12}=\omega_1+\omega_2$. Then $\nu_{12}=\nu_1+\nu_2$, and the value of the integral is

$$\frac{i_1+i_2}{\nu_{12}}=\frac{k_1\nu_1+k_2\nu_2}{\nu_1+\nu_2}e. \quad . \quad . \quad . \quad . \quad (2.5)$$

Provided $k_1=k_2=k_{12}$, this would give as the value of the integral, $k_{12}e$, leading to the result $k_{12}N_{12}e=n_{12}h$, already suggested in (1.11).

3. Prof. Darwin's Treatment for two Current Circuits.

The method of applying the quantum conditions employed in § 1 is unsatisfactory, because the system is one of two degrees of freedom, and so, according to accepted principles, cannot have more than two quantum numbers. I am indebted to Prof. C. G. Darwin for the following treatment, but have made slight alterations in his notation to suit the present case.

To quantize $$W=\tfrac{1}{2}a\dot{x}^2+f\dot{x}\dot{y}+\tfrac{1}{2}b\dot{y}^2, \quad . \quad . \quad . \quad . \quad (3.1)$$

where the cycles for x and y are from 0 to 1.

Put $$\left.\begin{aligned} p_x&=a\dot{x}+f\dot{y},\\ p_y&=f\dot{x}+b\dot{y}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

Then $$W=\tfrac{1}{2}\frac{bp_x^2-2fp_xp_y+ap_y^2}{ab-f^2} \quad . \quad . \quad . \quad . \quad (3.3)$$

The motion is therefore

$$\frac{dp_x}{dt}=-\frac{\partial W}{\partial x}=0, \text{ etc.}, \quad \dot{x}=\frac{\partial W}{\partial p_x}, \text{ etc.}, \quad . \quad (3.4)$$

or $$p_x=\text{constant}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.5)$$

Hence $\oint p_x\,dx=p_x$, as the x cycle is 0 to 1.

The quantization is thus

$$p_x=\tau_1 h, \quad p_y=\tau_2 h \text{ (where } \tau_1, \tau_2 \text{ are integers)}, \quad (3.6)$$

and $$W=\tfrac{1}{2}h^2\frac{(b\tau_1^2-2f\tau_1\tau_2+a\tau_2^2)}{ab-f^2} \quad . \quad . \quad . \quad . \quad (3.7)$$

Applying this method to the two current circuits, for which the electrokinetic energy is

$$W = \tfrac{1}{2}L_1 i_1^2 + M_{12} i_1 i_2 + \tfrac{1}{2}L_2 i_2^2$$

and the value of $\oint di$ over a complete period is κe (where κ is an integer), we find

$$\left.\begin{aligned} \kappa_1 e(L_1 i_1 + M_{12} i_2) &= \tau_1 h \\ \kappa_2 e(M_{12} i_1 + L_2 i_2) &= \tau_2 h \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3.8)$$

It has already been pointed out that $L_1 i_1 + M_{12} i_2$ or N_1 is the total number of magnetic tubes linked with the first circuit, and $M_{12} i_1 + L_2 i_2$ or N_2 is the total number of magnetic tubes linked with the second circuit. Thus the quantum conditions reduce to

$$\left.\begin{aligned} N_1 &= \frac{\tau_1}{\kappa_1}\left(\frac{h}{e}\right) \\ N_2 &= \frac{\tau_2}{\kappa_2}\left(\frac{h}{e}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.9)$$

As in the previous work the simplest interpretation which can be given to these results is obtained by assuming the existence of discrete quantum tubes of magnetic induction, the unit tube being defined by the value of h/e.

Reviewing the work of § 1 in the light of this more rigid treatment, it may be argued that the methods there employed are justified by the results obtained. The explanation of all the difficulties is to be found in the simple fact, illustrated in fig. 1, that the various magnetic tubes associated with two current circuits may be grouped together in several different ways. The relations between the different quantum numbers revealed by this discussion are suggestive in connexion with results derived from investigations on the complex structure of multiplets, especially as regards the Zeeman terms in strong and weak magnetic fields. Reference may be made to the work on this subject published in the past three years, principally by Landé, Pauli, and Sommerfeld.

4. Extension to any Number of Current Circuits.

In the case of a heavy atom Bohr's later theory postulates the existence of a large number of independent electron orbits. The work of Ellis and others suggests that quantum relations hold even within the nucleus, which may be composed of protons and negative electrons in orbital motion. On this view an atomic and also a molecular system is an

extremely complex system of orbits, in which positively or negatively electrified particles are circulating at high speed, thus virtually constituting a system of current circuits.

There is no great difficulty in extending the results for two current circuits, obtained in 1921 and given above, to the general case of any number of such circuits. For the electrokinetic energy of any system of currents is equal to one-half the sum of the strengths of each current multiplied by the total flux of magnetic force through its own circuit in the positive direction. Following out the same line of argument as before, it would seem that we are led again to the conception of quantum tubes of magnetic induction of strength h/e, and possessing electrokinetic energy of amount $\frac{1}{2}h\nu$, where ν is a frequency characteristic of the particular tube considered.

Instead, however, of writing down the equations for the general case and proceeding as in the previous section, it will be more instructive to consider a single Faraday tube of magnetic induction linked with n current circuits, $i_1, i_2, \ldots i_n$.

The energy associated with such a tube can be expressed as

$$\int \frac{\mu \mathrm{H}^2}{8\pi} \mathrm{A}\, ds \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

integrated over the length of the tube, where A is the area of the cross-section of the tube and ds is an element of its length. But μHA is constant along the whole length, so that the expression becomes $\frac{\mu \mathrm{HA}}{8\pi} \int \mathrm{H}\, ds$. The line integral of magnetic force along the length of the tube is

$$4\pi(i_1 + i_2 + \ldots + i_n),$$

so that the energy is given by

$$\mathrm{T} = \tfrac{1}{2}\mu \mathrm{HA}(i_1 + i_2 + \ldots + i_n). \quad . \quad . \quad . \quad (4.2)$$

We now assume that the quantum condition may be expressed in the form

$$2\int \mathrm{T}\, dt = nh \ (n \text{ integral}),$$

$$\text{or} \qquad \mu \mathrm{HA} \int (i_1 + i_2 + \ldots + i_n)\, dt = nh, \quad . \quad . \quad (4.3)$$

the integration for each current extending over the corresponding period *.

* It is hardly necessary to point out that this way of stating the quantum conditions is somewhat arbitrary, but so is any statement of these conditions, which must be regarded rather as a set of rules justified by the results obtained than as a consistent and unique theory.

This gives

$$\mu \mathrm{HA}(k_1+k_2+\ldots+k_n)e=nh. \quad . \quad . \quad . \quad (4.4)$$

Here, again, the simplest interpretation is to assume

$$n=k_1+k_2+\ldots+k_n,$$

so that the unit tube is defined by taking

$$\mu \mathrm{HA}=h/e. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.5)$$

The electrokinetic energy of the unit quantum tube in question is given by

$$\tfrac{1}{2}\frac{h}{e}(i_1+i_2+\ldots+i_n)$$

$$=\tfrac{1}{2}h(k_1\nu_1+k_2\nu_2+\ldots+k_n\nu_n), \quad . \quad . \quad . \quad (4.6)$$

since we may write

$$i_1=k_1e\nu_1,\ i_2=k_2e\nu_2,\ \ldots\ i_n=k_ne\nu_n.$$

Proper attention must, of course, be paid to the sign of each term.

Thus when $k_1=k_2=\ldots=k_n=1$, the electrokinetic energy of the unit tube

$$=\tfrac{1}{2}h(\nu_1+\nu_2+\ldots+\nu_n). \quad . \quad . \quad . \quad . \quad (4.7)$$

The importance of this mode of expression lies in the fact that *frequency* here plays the part of an additive quantity in formulating the energy of a system. This is a characteristic feature of Bohr's theory of spectral series, and in the next Section an attempt will be made to apply the result to the interpretation of Bohr's theory.

5. Application to the Theory of Spectral Series.

Sir William Bragg in the Kelvin Lecture * delivered before the Institution of Electrical Engineers on January 13, 1921, said: "The frequencies of the lines in a spectrum often display curious and exact numerical relations, in the form generally involving differences of frequencies of similar lines or groups of lines. . . .

"Now, there is nothing in our older conception of the origin of radiation within the atom to give us a clue as to why differences of frequencies should come into these empirical, though most useful, formulæ. We have pictured to ourselves vibrating systems, mechanical or electric, and waves arising therefrom. But what connexion between masses or electricities gives us in any simple way equations

* 'Nature,' cxcvii. pp. 82–109 (1921).

involving the addition or subtraction of frequencies? We are in a blind alley."

Even in Bohr's theory of spectral series the same difficulty is felt. But in his theory the bold step is taken of adopting as a basic principle in dealing with the emisson of radiation a relation between amounts of energy involving a linear relation between frequencies.

Bohr's theory of the origin of spectra is based on two fundamental assumptions:—

(1) An atomic system with an electron moving in a *stationary* orbit is associated with a definite amount of energy which can be calculated by employing the quantum principles in connexion with the laws of ordinary dynamics.

(2) When the atom passes from one stationary state to another, or the electron changes from one stationary orbit to another, there is an emission of *monochromatic* radiation of frequency ν_r determined by the relation

$$h\nu_r = W' - W, \quad . \quad . \quad . \quad . \quad . \quad (5.1)$$

where W corresponds to the initial, W′ to the final state of the system.

"Needless to say the founder of the new theory and his followers do not attempt to describe the mechanism of such an extraordinary performance, one, that is, that enables the atomic system to hit precisely upon the frequency ν_r required by the assumption" *.

The *kinematical* significance of Bohr's equation may be realized by expressing W in the form $\frac{1}{2}nh\nu$. The frequency of the radiation emitted is then given by

$$h\nu_r = \tfrac{1}{2}n'h\nu' - \tfrac{1}{2}nh\nu. \quad . \quad . \quad . \quad . \quad . \quad (5.2)$$

My object is to show that this relation can be interpreted by taking the frequency of the emitted radiation as identical with a definite frequency associated with a quantum tube or tubes of magnetic induction, such frequency being one characteristic feature of the system, both in its initial and in its final state.

In Part I. of this paper it has been shown that the integer n in the expression $W = \frac{1}{2}nh\nu$ may be interpreted as the total number of quantum tubes linked with the orbit of the electron, whether the orbit be a circle or an ellipse. Consequently, when, in Bohr's theory, a change takes place from one stationary state to another and n changes to n', there is an integral change in the total number of tubes linked with

* Silberstein, 'Report on the Quantum Theory of Spectra,' p. 6 (1920).

the orbit. When radiation is *emitted* there is a *diminution* in the number of these tubes equal to $n-n'$. But it is assumed in the theory that, whatever may be the value of $n-n'$, only one quantum of radiation is emitted. On the view now suggested it is natural to suppose that the radiated energy is the energy associated with a single quantum tube, the emission of radiation being a process consisting in, or consequent upon, the liberation of one quantum tube from the atomic system. It is, however, only when the electron passes between neighbouring orbits that the diminution in the number of tubes, $n-n'$, is equal to unity. In general, the decrease in the number of tubes linked with the orbit is more than sufficient to account for the single tube we have supposed separated from the system. If, then, we regard magnetic tubes as entities which can change in form, but cannot be created or destroyed * (so long, at least, as they are associated with an atomic system), we are forced to the conclusion that there must be some part of the system which can serve as a receptacle for the surplus tubes. Such a receptacle may be described as a "magneton," using that term in the wide sense I have advocated elsewhere † to denote that structure within the atom which may be regarded as the origin of the quantum magnetic tubes. We may employ the term without limiting ourselves to any precise model of the mechanism involved. It will cover the particular structure suggested by the term "ring electron," the more general case of the magneton of McLaren, or the "magnetic wheel" of E. T. Whittaker.

Consider the case of an atom consisting of a positive core and a negative electron. There are two possibilities presenting themselves. The core of the atom may be a magneton, as I have suggested in a previous paper on "An Atomic Model with a Magnetic Core" ‡, or the negative electron may be a magneton §.

Without entering into a discussion of these alternatives, it will be sufficient for our present purpose to assume that the magneton is closely associated with an integral number

* For an interesting discussion of the process of magnetization regarded as the opening out of molecular magnetic loops *which are already in existence*, and of the characteristics of such magnetic tubes of force, see Sir Oliver Lodge's lecture on "Magnetism and the Ether" (Journal of the Röntgen Society, xviii. July 1922).

† H. S. Allen, Proc. Roy. Soc. Edin. xlii. p. 213 (1922).

‡ H. S. Allen, Phil. Mag. xxix. p. 714 (1915). See also a paper by Th. Wereide, *Ann. d. Physik*, xlix. p. 966 (1916).

§ "The Case for a Ring Electron," Physical Society of London, Proceedings, xxxi. p. 49 (1919).

of quantum tubes of frequency ν_r. As in Bohr's theory the electron is supposed to describe an orbit about the nucleus, the size of the orbit and the frequency being determined by the usual quantum relations. For simplicity we shall consider the case of a massive nucleus, which may be regarded as at rest.

Let n denote the number of quantum tubes linked with the orbit and also passing through the magneton, and n_r the number of quantum tubes associated with the magneton which are not linked with the orbit.

Then, in accordance with the principles discussed in the earlier portion of this paper, the electrokinetic energy of the system in its initial state is given by

$$T=\tfrac{1}{2}n_r h\nu_r+\tfrac{1}{2}nh(\nu+\nu_r). \quad . \quad . \quad . \quad . \quad (5.3)$$

Denoting the corresponding quantities in the final state by accented letters, we have, similarly,

$$T'=\tfrac{1}{2}n_r' h\nu_r'+\tfrac{1}{2}n' h(\nu'+\nu_r'). \quad . \quad . \quad . \quad (5.4)$$

To proceed further we have to make some specific assumptions with regard to the frequencies. In the first place, we assume that the frequency ν_r remains unchanged in passing from the initial to the final state, and we identify this frequency with that of the emitted radiation.

In systems which emit hydrogen-like spectra the kinetic energy is numerically the same as Bohr's W. In his theory the kinetic energy in the new orbit is greater than that in the old, but the amount of potential energy set free is exactly twice the change in the kinetic energy. Consequently, an amount of energy is available for radiation which is equal to the change in the kinetic energy. This is

$$T'-T=\tfrac{1}{2}[(n_r'+n')-(n_r+n)]h\nu_r+\tfrac{1}{2}n'h\nu'-\tfrac{1}{2}nh\nu. \quad (5.5)$$

We now assume that in the change from one state to the other *one* quantum tube has been liberated from the magneton, and put

$$\tfrac{1}{2}h\nu_r=T'-T. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.6)$$

Hence

$$\tfrac{1}{2}h\nu_r=\tfrac{1}{2}[(n_r'+n')-(n_r+n)]h\nu_r+\tfrac{1}{2}n'h\nu'-\tfrac{1}{2}nh\nu. \quad (5.7)$$

But if a single quantum tube is liberated, the total number of bound tubes in the initial state is one greater than the total number in the final state, *i. e.*,

$$n_r+n=n_r'+n'+1. \quad . \quad . \quad . \quad . \quad (5.8)$$

Thus the above equation reduces to

$$h\nu_r=\tfrac{1}{2}n'h\nu'-\tfrac{1}{2}nh\nu, \quad . \quad . \quad . \quad . \quad (5.9)$$

which is identical with that employed by Bohr.

It should be observed that in this theory the electron may be regarded as forming one member of a coupled system, and with each "bound" electron *at least two* frequencies are associated. The first of these, ν_r, has been assumed the same in the initial and final state of the system, and identical with the frequency of the emitted radiation. The second frequency, ν, is that on which the "binding" of the electron to the rest of the atom depends. Thus the frequency ν_r corresponds to that met with in the classical electromagnetic theory of absorption and dispersion, whilst the frequency ν is identical with that found in the theory of Bohr and Sommerfeld. Whilst in one sense it is not possible to "reconcile" the quantum theory with orthodox dynamics, the suggestions now put forward serve to indicate the possibility of a connexion between the two points of view, and even to show the general nature of the relationship.

It may be objected that the foregoing presentation implies that as the frequency of the monochromatic radiation is identified with the frequency of the magneton, that frequency is predetermined and there must be as many different atoms as there are lines in a spectral series. This objection carried more weight with me in 1921 than it does at the present time, because Prof. Whittaker has shown clearly by means of his quantum mechanism (1922) how frequency may be varied in an atomic model, whilst the number of magnetic tubes remains constant. In the present case, we may suppose that the frequency of the magneton itself may assume *any* value, but the catastrophic emission of radiation will occur when, and only when, the frequency assumes the particular value required by Bohr's equation.

6. Summary and Conclusion.

In earlier papers the hypothesis, first suggested by A. L. Bernoulli*, of the existence of discrete tubes of magnetic induction determined by the ratio of Planck's constant h to the charge e of an electron, has been applied to the case of an electron moving in a circular or an elliptic orbit. In this paper more complex distributions are considered. Two magnetons or two electron orbits may be represented by two current circuits carrying currents i_1 and i_2. The quantum conditions applied to this case are most simply interpreted by the same hypothesis of the

* Bernoulli, *Archives des Sciences*, xlii., p. 24 (1916).

atomicity of magnetic tubes. The electrokinetic energy of a quantum tube is given by $\frac{h}{8\pi e}\Sigma H ds$. When the tube is linked with two current circuits, $\Sigma H ds = 4\pi(i_1+i_2)$, assuming the tube passes through each circuit in the positive direction. Thus the electrokinetic energy associated with the tube is $\frac{1}{2}\frac{h}{e}(i_1+i_2)$. When each circuit is equivalent to a single electron revolving in an orbit with assigned frequency (ν_1 or ν_2), this reduces to $\frac{1}{2}h(\nu_1+\nu_2)$, or we may write it $\frac{1}{2}h\nu$, where ν is a frequency characteristic of the tube under consideration. It is tempting to suppose that the frequency ν appropriate to a particular tube corresponds to the frequency of a state of spin or vorticity associated with that tube. But the question as to whether such vorticity represents the actual physical state of the tube need not at present be discussed.

Incidentally, a mechanical model is described, which gives a very close representation of the electrical system of two current circuits.

The quantum relations are applied to the general case of any number of current circuits, and it is shown that there is no difficulty in generalising the previous results. It is pointed out that in this mode of formulating the energy of a system, frequency plays the part of an additive quantity. As this is a characteristic feature of Bohr's theory of spectral series, an attempt is made to apply the result to the interpretation of Bohr's theory. It is shown that Bohr's frequency relation

$$h\nu_r = \tfrac{1}{2}n'h\nu' - \tfrac{1}{2}nh\nu$$

can be interpreted by taking the frequency ν_r of the emitted radiation as identical with that of a quantum tube or tubes, such frequency being characteristic of the system both in its initial and in its final state. Although the suggestions put forward do not abolish the conflict between the quantum theory and classical dynamics, they may serve to show more clearly the points of contact between the two theories. It may at least be said that a further step has been taken in the magnetic interpretation of the quantum.

University of St. Andrews,
June 7, 1924.

XLVII. *Gas Ion Mobilities and their Independence of the Nature of the Ion.* By Leonard B. Loeb*.

SINCE 1916 the writer (1) has at various times attempted by means of crucial experiments to distinguish between the so-called classical theory of the "cluster ion" in gaseous ionization phenomena and the "small ion" theory of Sutherland (2) and Wellisch (3). In all cases these supposed crucial experiments gave results that were, while suggestive of a small ion interpretation, never decisively in favour of either theory. In 1917 (4) the writer summarized the field as a whole, and showed that as regards most of the ion phenomena the explanations on either theory were equally good. A knowledge of the nature of the ion is of value as it may throw considerable light on the law of forces acting between molecules and charges, and as it may have some bearing on the interpretation of ionization phenomena in solutions.

In a recent (5), but futile, attempt to distinguish between the two theories based on measuring the mobilities of ions in mixtures of dry ammonia gas and air, the writer found that the mobilities of the ions varied inversely as the square root of the product of the molecular weight of the gas into the dielectric constant of the gas diminished by unity. Such a variation of mobility with the dielectric constant of the gas does not agree with Wellisch's (3) equation for the mobility of a small ion, in which the mobility varies inversely as the first power of a term of the form $(1+b\,(D-1))$, where b is a constant. By introducing a term for the shortening of the mean free path assuming a cluster ion (whose size could be estimated according to a theory of Langevin (7) based on an inverse fifth power law of force) into the mobility equation of Langevin (6) for a cluster ion in a somewhat questionable way, the writer obtained an equation in which the mobility varied approximately inversely as the square root of the dielectric constant diminished by unity.

Recently Sir J. J. Thomson (8) has published a theoretical treatment of the question of the change of the mean free path of an ion in virtue of the forces it exerts on neutral molecules. This treatment is quite rigorous and is based on the assumption of an inverse fifth power law of force (that is, such a law of force as a charged body would exert on a neutral dielectric body of a dielectric constant D). Thomson also shows how the resulting equation must be modified in

* Communicated by the Author.

case an inverse cube law of force had been assumed (that is, in case one assumed that the attraction of the ion was that of a charged body on a molecular dipole). It can be shown that if this shortening of the mean free path computed by Thomson on an inverse fifth power law be introduced into the Langevin (6) equation for ionic mobilities, and if the shortening be ascribed to the force of attraction of an ionic charge on a gas molecule whose dielectric constant in bulk is D, the mobility will vary inversely as the square root of the product of the mass of the gas molecules into the dielectric constant diminished by unity, as found by experiment.

On introducing the factor for shortening the mean free path of an ion due to the charge, mentioned above, into the Langevin (6, 9) mobility equation which in its method of derivation is consistent with the Thomson theory, certain very interesting transformations of the equation for the mobility of the ions occur. The transformations are such *that they not only practically completely eliminate any factor involving a specific hypothesis of the nature of the ion from the equation, thus making it impossible from mobility measurements to decide upon the nature of the ions*: but furthermore, the resulting equation so completely predicts qualitatively, and even quantitatively, most of the characteristic phenomena exhibited by ions that it merits a fuller discussion. It will be the purpose of this paper to set forth briefly the various phenomena to be explained by any theory of ionic mobility and the manner in which this theory explains them.

For a charged particle of mass m moving in a gas whose molecules have a mass M, with a relative velocity V, J. J. Thomson (8) finds that the mean free path of the charged particle is to that of the uncharged molecule as

$$\frac{\lambda'}{\lambda} = \frac{1}{2\cdot 2\left(\dfrac{2k}{\sigma^4}\dfrac{\mathrm{M}m}{\mathrm{M}+m}\mathrm{V}^2\right)^{\frac{1}{2}}}.$$

Here k is the force constant of the attraction between the ion and the molecule. At present it is hard to be sure of the exact value of this force constant. But one might assume, as Langevin (7) has done, that the molecules act like dielectric bodies such that in the field produced by an ion they are acted on by a force

$$\mathrm{F} = \frac{(\mathrm{D}-1)e^2}{2\pi n_0 r^5}.$$

Here D is the dielectric constant of the gas in bulk; n_0 is

the number of molecules per c.c. under the conditions pertaining to the measurement of D; e is the electron; and r is the distance of the centre of the ion from that of the molecule. Thus k becomes $\frac{(D-1)e^2}{2\pi n_0}$. In the equation of Thomson, the quantity σ is the sum of the radii of the ion and the molecule and corresponds to the average distance of approach on impact. V is the relative velocity of approach of the ion and molecule, and the quantity $\frac{mM}{M+m}V^2$ is for the present purposes none other than twice the kinetic energy of agitation of the gas molecules at the temperature of the gas, from the definition of this quantity as used by Thomson. It may consequently be replaced by Mc^2 in the equation. Thus one can write:

$$\lambda' = \frac{\lambda}{2{\cdot}2\left\{\frac{2(D-1)e^2}{2\pi n_0 \sigma^4 M c^2}\right\}^{\frac{1}{2}}}$$

where c is the square root of the average square speed.

Langevin (6, 9) deduced an equation for the mobility of a complex cluster ion of mass m among gas molecules of mass M on the basis of the kinetic theory of gases assuming no forces to act between the ions and the neutral molecules. This equation takes the form:

$$K = {\cdot}815\,\frac{e}{M}\,\frac{\lambda'}{c}\sqrt{\frac{M+m}{m}}.$$

Here λ' is the mean free path of the ion cluster. Since, as J. J. Thomson points out, his factor for the reduction of the mean free path of an ion due to its attractive forces is independent of an assumption of a cluster theory or not, one can introduce * the Thomson factor for the shortening of the mean free path into Langevin's equation †.

* This is subject to one restriction, however, and that is, that the Thomson factor, because of its derivation, cannot be used where it is less than unity.

† This may seem a questionable procedure, but short of a very complicated and tedious analysis and re-derivation of Langevin's equation introducing attractive forces into it, the matter cannot be treated rigorously. As the results seem to justify this procedure the fault committed is not as serious as it would be on a strictly theoretical basis.

The combined equations then take the form :

$$K = \cdot 815 \frac{e}{mc} \frac{\lambda}{2 \cdot 2 \left\{ \frac{(D-1)e^2}{\pi n_0 \sigma^4 M c^2} \right\}^{\frac{1}{2}}} \sqrt{\frac{M+m}{m}}.$$

If now, the value for λ from the kinetic theory of gases, to wit, $\lambda = \frac{1}{\pi \sqrt{2} n \sigma^2}$ be placed in the combined equations, the equation reduces to the form :

$$K = \frac{\cdot 815}{2 \cdot 2 \sqrt{2\pi}\, n M^{\frac{1}{2}} (D-1)^{\frac{1}{2}} n_0^{\frac{1}{2}}} \sqrt{\frac{M+m}{m}}.$$

This can be still further simplified by replacing n the number of molecules per c.c. of the gas in which the ions are moving by $n_0\,(p/760)$, where p is the pressure in mm. of mercury, by replacing M by $M_0\mu$ where μ is the mass of an atom of hydrogen, and M_0 is the molecular weight, and by writing that $m = bM$, so that the final form of the equation is :

$$K = \frac{\cdot 815 \sqrt{\frac{M+m}{m}}}{2 \cdot 2 \sqrt{2\pi} (\mu n_0^{\frac{1}{3}}) M_0^{\frac{1}{2}} (D-1)^{\frac{1}{2}} \frac{p}{760}}$$

or better :

$$K = \frac{A \sqrt{\frac{1+b}{b}}}{\frac{p}{760} \sqrt{(D-1) M_0}},$$

where A is a constant depending on the Avogadro number, the mass of an atom of hydrogen, and a numerical coefficient.

This striking transformation of the ion mobility equation is now capable of verification on the basis of its ability to predict the properties of the gas ions. This will be done in what follows.

I. *Mobility and the Size and Mass of the Ion.*

It is seen at once that the equation for the mobility of the ion is independent of both the size and the mass of the ion except for the small factor $\sqrt{\frac{1+b}{b}}$. This varies in value

from 1·42 for a single small ion ($b=1$) to unity for a very large cluster for which b is great compared with unity.

1. It had long ago been shown by Franck (10) that the mobility of radioactive recoil atoms in hydrogen was about the same as that of normal ions in hydrogen, although their mass was considerably above that of the hydrogen molecules. Likewise Wellisch (11) had shown that the mobility of methyl iodide ions in hydrogen was the same as that of hydrogen ions in hydrogen in spite of their difference in mass. In neither of these experiments was the precision very high, and it is very doubtful whether the effect of the factor b in the equation above could have been detected in these experiments. Thus, their results are predicted by the new theory, a feat that no theory heretofore has succeeded in doing without further assumptions.

2. The values of the mobility of gas ions seems to be completely independent of any factor related to the diameter of the ions or the gas molecules. The writer had for a long time wondered at the failure to obtain any correlation of mobility with molecular or ionic diameters, although this factor appears in all mobility equations, and although it varies very widely from gas to gas. The new theory leads one to expect this independence.

3. The equation also shows that from the ionic mobilities alone, except for the small variation due to b, *it should be impossible to determine the nature of the ion from any mobility experiments.* It is for this reason that the previous attempts to distinguish between the cluster and small ion theories on the basis of crucial experiments on the part of the writer and other workers have always yielded indecisive results. Thus, the writer (1) and Professor Yen (12) attempted to distinguish between the theories by measuring mobilities in very high electric fields, where owing to their high kinetic energies the cluster ions should have broken up. The experiments showed no change in mobility, while on a cluster theory the mobility should have increased about fourfold, and on a small ion theory it should have decreased by a factor of about 0·4.

4. The small change of mobility for a change in mass of the cluster represented by the factor containing b should, however, on careful measurement, become manifest every time the ion permanently changes its size. It is perhaps on the basis of such a change that the reduction of the mobility of the positive ions in nitrogen, hydrogen, and air, with age, discovered by Erikson (13) and confirmed by Wahlin (14), as well as the difference in mobility of +

and — ions, may be explained. If one assumes that the negative ion is a single charged molecule carrying an extra electron and on formation the positive ion is likewise a molecule that has lost an electron, but that with age the *positive ion* adds a cluster of five molecules around it, then its initial mobility which equals the negative will, when it has added its five molecules, be reduced from 1·8 cm./sec., which it has as a new ion, to 1·4 cm./sec. This corresponds to a change in the value of $\sqrt{\frac{1+b}{b}}$ from 1·42 to 1·09, which takes place for a change in b of from 1 to 5.

If the mass of the ion became very small, as for example in the case of an electron in a gas, the present theory would hardly be applicable. For in that case the electron picks up energy from the field, making the factor of J. J. Thomson approach unity, so that the shortening of the mean free path ceases to count and the equations of K. T. Compton (15) may be applied.

II. *The Mobilities of the Ions and Pressure.*

The mobility of positive ions has been shown to vary inversely with pressure for pressures ranging from a few tenths of a millimetre to close to 100 atmospheres (16, 17). The same holds true for the negative ions at higher pressures; and, as shown by Wellisch (18) and confirmed by Loeb (19), for the lower pressures, *provided the electrons are given time to attach to molecules to form ions before they enter the measuring field.* Otherwise ionic mobilities are not measured, the mobilities obtained corresponding to carriers part ion and part electron of very widely different mobilities (28, 29). At the higher pressure ranges, above 66 atmospheres, the mobilities decrease a little less rapidly than the inverse pressure law would demand according to McLennan (17). The significance of this effect is completely obscure at present, and it is too small an effect in any case to merit a longer discussion at this point. As is seen, the general behaviour is predicted by the equation through the factor $p/760$ in the denominator.

III. *The Mobility and the Mass of the Gas Molecules in which the Ion moves.*

Long ago, Kaufmann (20) stated that for the more "permanent gases," the mobility varied inversely as the square root of the molecular weight of the gas in which the ion moved. This rule, known as Kaufmann's rule, was extended

by Loeb (4) to the case of all gases and vapours provided a correction factor involving the dielectric constant of the gas was applied. It had been predicted by the older ionic mobility equations, such as the Langevin equation, since the factor e of that equation varies as the square root of M. In order to make the equation hold, however, it became necessary to assume that K was independent of all factors other than mass and dielectric constant, as one went from gas to gas. This seemed absurd in view of the fact that the equations also contained the factor λ. As is seen, the present theory predicts that outside of a variation with D and p, the mobility should only vary inversely as the square root of M.

IV. *The Mobility and Temperature.*

All previous theories of ionic mobilities had predicted that as the mobility varied inversely as e it should vary inversely as the absolute temperature of the gas. Although the results of different mobility measurements do not completely agree as to the exact amount of variation of mobility with temperature, all the observers agree in finding *very little change with temperature*. Sutherland (21), in analogy with his treatment of the disagreement of the observed and predicted variation of gaseous viscosity with the temperature, derived an equation giving the change in ionic mobility with temperature. The theory fitted the observed results of Phillips (22) quite well. Erikson (23), in some very careful work at constant density, found that the mobility was independent of temperature down to nearly liquid air temperatures, where the mobility showed a decrease of about 10 per cent. The present theory leads one to expect that K will be independent of temperature. This agrees better with the experimental facts than any other theory. At the lowest temperatures the mobilities and their variations need further study and measurement.

The same reasoning would explain why it was that the writer (1) and Professor Yen (12) failed to find the expected decrease in mobility of the ions in high electrical fields, which, as was stated above, should have been a reduction by a factor of 0·4. A decrease of this sort was expected because owing to the high fields the average velocity of the ion was about 2·5 times the velocity of thermal agitation of the gas molecules. In such a case, with the combined Thomson and Langevin equations, the factors e become the

velocities of the ions and cancel out as they do in the case of ions in temperature equilibrium with the gas. Thus the new equation applies to this case and we see why the experiment yielded an indecisive result.

V. *Mobilities and the Dielectric Constant of the Gas.*

It had been pointed out in 1917 (4) that the ionic mobilities varied from gas to gas inversely as a product of the fourth root of the dielectric constant of the gas diminished by unity, multiplied by the square root of the molecular weight. This relationship, independent of any theoretical foundation, seemed to hold fairly well even with the large variations of the sources from which the data came. Recently the writer (5) has shown that for a set of measurements made under identical conditions in mixtures of NH_3 gas and air the mobility varied much more closely according to the inverse square root of the average dielectric constant of the mixture diminished by unity. The suggested combined equations of Thomson and Langevin lead to a variation in agreement with the later measurements. This variation is distinctly different from the variation with the inverse fourth root of $D-1$, and would cause a poorer agreement in a table such as reproduced in the earlier (4) paper than there was found originally. It must be pointed out that the table there given is based on the very diverse results of mobility measurements by different observers using different methods. Thus, the values are not consistent and it is not surprising that the agreement is not good. For example, the value for K in air was formerly taken as 1·4 relative to the value ·74 for NH_3. The recent measurements made under identical conditions in both cases give the relative values of K as 1·6 for air against ·52 for NH_3. This result is much more consistent with the Langevin-Thomson theory than with the empirical rule previously laid down. Before one can accept the new theory as established in this regard, one must, however, be able to extend the ammonia-air measurements to a number of other gases.

In gases which have a markedly polar nature, *i. e.* those that have permanent electrical moments of their own, such as HCl, the force acting should be the inverse third power law. Such a law, according to J. J. Thomson, should have the force factor k (*i. e.* $D-1$) acting in the denominator in the first power. It would be of considerable importance to test this out experimentally, and such experiments are now being undertaken.

VI. *Electron Attachment and the Theory.*

The writer (24) has shown that in its broad aspects the theory of negative ion formation proposed by J. J. Thomson (24) is able to predict the observed phenomena of attachment of electrons to molecules of gases quite successfully. This theory assumes that the electron does not attach to the molecule on its first impact, but that it does so in general after n impacts with molecules, where n is a constant depending on the chemical nature of the gas only. This idea is elaborated further by J. J. Thomson (25) in the recent paper in which the theory of the change of the mean free path for charged molecules is discussed. He shows that it follows naturally from the considerations such as lie at the basis of the theory proposed, and that the predicted value of n for air is of the same order of magnitude as the observed. This theory would make it appear that the electrons did not attach unless their energy were low and would lead one to expect a variation with the nature of the molecules as is observed. It might be pointed out that Bailey (26) recently also suggested that the attachment was limited to electrons of low velocity.

It seems to the writer, however, that the type of theory as applied by J. J. Thomson to the treatment of the combination of electrons and molecules would be less likely to hold on the modern theory of atomic structure, than it would for the junction of ions and molecules. It seems likely that on the Bohr theory the electron would not attach to a molecule to make a negative ion unless it struck the molecule in such a manner and under energy conditions such that it could assume a stable orbit about the molecule consistent with the rest of the molecule's electronic system. It is significant that the molecular types noted for the stability of their electronic system (*e.g.*, as suggested by G. N. Lewis, 27) are those that apparently never attach an electron at all. It is further very certain from measurements that the electron once attached does not leave the molecule again. This points to a very stable union. It also seems possible from the experiments of Erikson (13) and Wahlin (14) that the positive ions consist of very stable aggregates of molecules, about a molecule rendered unstable by itself through the loss of an electron. In any case, the proposed theory is in no way inconsistent with the attachment results, while the possibility of the formation of more stable aggregates must be considered.

VII. *Ions and Condensation.*

As was pointed out in 1917 (4), the condensation of supersaturated vapours on ions is in no way essentially connected with any theory of ionic behaviour. All that is needed is that an unstable droplet that would evaporate under given conditions of supersaturation should pick up an ion, as do Millikan's oil drops, in order to grow to a visible size as indicated by the theory of J. J. Thomson (30).

Evaluations of Gas Ion Mobilities from the New Theory.

Numerically, the mobilities of the ions may be computed for any gas from the equation deduced, by taking the values of M_0 and D from tables, evaluating the constant A, and assuming a value of b. If the resulting quantity be divided by 300, the mobility is given in cm./sec. per volt./cm. A table of values computed for a number of gases follows, assuming $b=1$. It must be noted that the observed values are some of them very old values, and that they represent measurements made in diverse manners. The values of K in the vapours of the less volatile substances are most likely to be in error since here the technique of measurement is not so simple.

Gas.	M_0.	D−1.	$(D-1)M_0$.	K computed. $\frac{1{\cdot}04\times10^{-1}}{\sqrt{(D-1)M_0}}$.	K observed.
H_2	2	$2{\cdot}73\times10^{-4}$	$2{\cdot}34\times10^{-2}$	4·43	6·02
He	4	$0{\cdot}74\times10^{-4}$	$1{\cdot}72\times10^{-2}$	6·02	5·09
A	40	$1{\cdot}0\times10^{-4}$	$6{\cdot}33\times10^{-2}$	1·64	1·37
Air	28·8	$5{\cdot}9\times10^{-4}$	$13{\cdot}1\times10^{-2}$	0·79	1·35−1·6*
NH_3	17	$77{\cdot}0\times10^{-4}$	$36{\cdot}2\times10^{-2}$	0·29	0·74−·52*
CO_2	44	$9{\cdot}6\times10^{-4}$	$20{\cdot}6\times10^{-2}$	0·51	0·81
CO	28	$6{\cdot}9\times10^{-4}$	$14{\cdot}0\times10^{-2}$	0·74	1·10
SO_2	64	$90{\cdot}5\times10^{-4}$	$76{\cdot}2\times10^{-2}$	0·14	0·44
N_2O	44	$10{\cdot}7\times10^{-4}$	$21{\cdot}8\times10^{-2}$	0·48	0·82
C_2H_5OH	46	$94{\cdot}0\times10^{-4}$	$66{\cdot}0\times10^{-2}$	0·16	0·34
CCl_4	154	$42{\cdot}0\times10^{-4}$	$80{\cdot}5\times10^{-2}$	0·13	0·30
C_2H_5Cl	65·5	$155{\cdot}0\times10^{-4}$	$101{\cdot}0\times10^{-2}$	0·10	0·33
$C_4H_{10}O$	74·0	$74{\cdot}2\times10^{-4}$	$74{\cdot}2\times10^{-2}$	0·14	0·24

* These values recently measured under the same conditions by writer.

It can be seen that the mobilities computed are of the right order of magnitude and do not differ widely from the observed values in some cases. In the vapours of high dielectric constant the deviation between observed and computed values is the greatest. Notwithstanding these deviations, the evaluation of the ionic mobility from such apparently unexpected quantities, which are independent of mean free path and charge, and which fit the experimental values better than any other ion theory, must impress one with the plausibility of the theory underlying it.

VIII. *Conclusions.*

From the foregoing, one may safely conclude that the combined Thomson-Langevin equations as presented furnish us with a theory of ionic behaviour that predicts better than any single theory heretofore proposed the behaviour of the gas ions under various conditions. It is further seen that the theory shows that except for the effect of the factor $\sqrt{\frac{1+b}{b}}$ there is no quantity in the mobility equation which permits one to decide on the nature of the ion. Thus, except for this feature, all attempts to distinguish between a cluster and a small ion theory on the basis of mobility measurements are futile.

While the theory is applicable to either type of ion theory, as J. J. Thomson points out, the assumption of an inverse fifth power law leads to the use of the term

$$2{\cdot}2\left(\frac{2k}{\sigma^4\,\frac{Mm}{M+m}\,V^2}\right)^{\frac{1}{3}}$$

for the shortening of the mean free path which must be less than unity in order that the mean free path begin to be decreased. This means that when

$$2{\cdot}2\left(\frac{2k}{\sigma^4\,\frac{Mm}{M+m}\,V^2}\right)^{\frac{1}{3}}$$

becomes greater than unity the value of the potential energy of the molecule at a distance σ from the ion $\left(\frac{k}{4\sigma^4}\right)$ is greater than the kinetic energy of agitation of the molecules and ions, $\left(\frac{1}{2}\,\frac{Mm}{M+m}\,V^2\right)$. Such a relation is also the condition for

a cluster formation. Thus, as J. J. Thomson shows later in his paper, the ion on the average forms a cluster and dissociates it again all along its paths. This formation and dissociation forms a labile cluster which one is unconscious of as far as the mobility measurements are concerned. Thus, the mobility of the ion is not just that of a single charged molecule, but varies from it by the quantity depending on the value of b. The variation is small. Since, owing to the statistical nature of the cluster formation, some ions have more than their share of clustering during a measurement while others have less, the factor $\sqrt{\frac{1+b}{b}}$ should cause a slight variation of K about the mean value of K for the ions. This would produce asymptotic portions to the curves obtained in determining ionic mobilities in experimental measurement. Such asymptotic feet have always been observed, but since such feet could also be caused by instrumental irregularities it becomes impossible to test the theory on this basis. To explain the Erikson-Wahlin (13) (14) effect, it becomes further essential to this theory to assume that under some circumstances the clustering may take a more permanent form than suggested by Thomson. That this should occur for a molecule that is rendered unstable through the loss of an electron would not be surprising.

Thus the theory of Thomson, when combined with the theory of Langevin, clears up much that is obscure in the behaviour of gas ions, puts an end to the futile cluster-small ion theory controversy, tells what law of force is exerted by the ion on the majority of gas molecules, and yields an adequate theoretical background to guide the future workers in the field.

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XLVIII. *On the Escape of Heat from the Earth's Crust.* *By* J. R. Cotter, *M.A.**

IN two recently-published papers (Phil. Mag. Ser. 6, vol. xlv. No. 270, June 1923, and vol. xlvi. No 271, July 1923) Prof. Joly has given an account of his theory of the causes which produce the great geological revolutions. The present paper is an attempt to determine mathematically the temperature changes which occur in the sub-oceanic parts of the earth's crust after the close of a revolution. The preliminary sketch of the processes which are assumed to take place is based partly on the papers above referred to, and partly on an explanation of the theory verbally communicated by Prof. Joly, who has also supplied me with all the numerical data which are here made use of.

According to Prof. Joly's theory, that portion of the earth's crust immediately beneath the ocean-floor consists of basalt, in which a continual generation of heat takes place, owing to the presence of radioactive materials. Prof. Joly concludes on experimental grounds that the heavier ultra-basic materials which probably underlie this stratum of basalt are much less radioactive. For the purpose of simplifying the investigation, I shall assume that no transmission of heat

* Communicated by the Author.

occurs through that horizon which may be regarded as the lower boundary of the basalt. The modifications which would have to be made in the theory when the radioactivity of the underlying rock is taken into account need not here be considered. The temperature of the upper surface of the basalt will be taken to be 0° C., which is approximately the temperature of the ocean-floor.

Let us suppose that at some stage in the history of the earth's crust the basalt is solid throughout. As we descend from the upper surface, the temperature will rise until at a certain depth the melting-point of basalt is reached. If we denote the melting-point by θ_0, then we may call this horizon the θ_0 geotherm. Below this level the rock is supposed to be everywhere at its melting-point. The temperature will not be quite uniform, but will increase slowly with depth, since the melting-point of basalt rises with increasing pressure. A long period of quiescence will ensue, during which the radioactive heat generated above the θ_0 geotherm will escape by conduction through the ocean-floor, while below this geotherm the heat generated will become latent owing to liquefaction of the rock, the temperature remaining steady all the time. It seems probable that the material in this lower portion would preserve its rigidity till an advanced stage of liquefaction has been reached, being in a condition somewhat resembling that of a sponge filled with water. A period of activity would now set in, starting with the breakdown of the weakened material owing to the disruptive action of tidal forces. Circulation might begin slowly, but would rapidly increase, because the descending portions would tend to solidify owing to increase of pressure, so that the increase of density due to solidification would accelerate the rate of descent; while the ascending portions would become more fully liquefied and would rise faster. As soon as circulation became general, a precipitate of solid material would begin to be formed at the bottom of the liquid mass; while at the same time the rest of the medium, up to the θ_0 geotherm, would become quite fluid, its temperature being nearly uniform and equal to the temperature of the solid deposit—that is, the temperature of the melting-point of basalt at a pressure equal to that of the fluid at its lowest level. Thus the upper part of the fluid would be above the melting-point appropriate to its pressure, and it would begin to melt away and erode the solid rock above it—that is, it would push the θ_0 geotherm upward. This process would be comparatively rapid at first, but would fall off owing to two causes: first, because as the fluid became

shallower owing to the deposit of solid, its temperature would fall, and secondly, because the loss of heat by conduction through the ocean-floor would become accelerated as the geotherms rose. Prof. Joly thinks that the θ_0 geotherm would rise to within a very few miles of the surface. It would, however, finally become stationary and then descend. At this stage the escape of heat would be very rapid, and the rate of solidification at the bottom would also be rapid. There seems little reason to doubt that the whole would eventually become solid again, and cooling would go on till it recovered its initial condition and initial distribution of temperature. The whole series of changes would form a cycle, which would be repeated.

It would not be easy to determine the rate at which the θ_0 geotherm would rise, but an approximate estimation of the rate at which it would fall can be made, and this is the object of the present paper.

In the first place, it is necessary to observe that there is a maximum depth, below which this isotherm cannot fall. This depth, which will be denoted by the letter l, is such that it is just possible for all the heat generated by radioactive agency to pass upward by conduction when no access of heat takes place from below. This depth, as calculated below, is about 30·6 miles. Neglecting, for the sake of simplicity, the variation of the melting-point of basalt with pressure, we may take this melting-point θ_0 to be a constant and equal to 1150° C. This assumption implies that no conduction of heat takes place below the θ_0 geotherm. If we represent distance measured vertically downward from the ocean-floor by x, then we may confine our attention to the stratum between the two horizontal planes $x=0$ and $x=l$, the former being kept at zero temperature, and the latter being regarded as a boundary impervious to heat. Since we do not know the initial position of the θ_0 geotherm, it will be convenient to assume that it starts from the ocean-floor. It will be seen that this assumption can make little difference in the time estimate, as the initial cooling would be very rapid.

We have now a perfectly definite mathematical problem to solve. Given a uniformly radioactive medium bounded by the parallel planes $x=0$ and $x=l$, it is required to find the distribution of temperature at any time t, the upper surface being maintained at zero temperature and the lower being impervious to heat, the whole being initially solid and at the temperature of the melting-point. We must know the radioactivity, conductivity, specific heat, and density.

For our purpose, the only difference between sensible heat and latent heat is that the latter is not conducted. It will therefore make no difference in the solution of the problem if we suppose that the substance does not melt, and that its temperature may rise above θ_0, provided that we also make the assumption that the conductivity is zero everywhere below the θ_0 geotherm. Even in this form, the mathematical difficulties of the problem are so formidable that it does not seem possible to solve it. This is due to the fact that the plane which separates the upper conducting portion from the lower non-conducting part is a moving plane, the rate of movement of which has to be determined by the solution of the equations. In these circumstances I have been compelled to make the further assumption that the conductivity is uniform throughout. Some remarks will be made later on the nature of the error introduced by this assumption.

The simplified problem may now be stated as follows :— Given a medium whose radioactivity is such that the temperature in insulated material would rise a degrees per second, and whose diffusivity (Maxwell's thermometric conductivity) is κ, required to determine the temperature distribution at any time t, if the initial temperature is θ_0 throughout, and if the medium is contained within two fixed parallel planes $x=0$ and $x=l$, of which the former is maintained at zero temperature, while the latter is impervious to heat.

The differential equation of conduction for a non-radioactive medium would be

$$\frac{\partial\theta}{\partial t} = \kappa\frac{\partial^2\theta}{\partial x^2}.$$

If the medium is radioactive, the rate of rise of temperature $\partial\theta/\partial t$ is increased by an amount a, so that the equation becomes

$$\frac{\partial\theta}{\partial t} = \kappa\frac{\partial^2\theta}{\partial x^2} + a. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation reduces at once to the preceding form if we put $\theta = v + at$. The solution of this is well known. As written below, it is merely a special case of a more general solution which I have taken from H. S. Carslaw's 'Fourier's Series and Integrals,' § 103 (1st ed. 1906). The required solution is

$$\theta = \frac{ax(2l-x)}{2\kappa} + \frac{4}{\pi}\Sigma'\frac{1}{n}\left(\theta_0 - \frac{4al^2}{n^2\pi^2\kappa}\right)e^{-\frac{n^2\pi^2\kappa t}{4l^2}}\sin\frac{n\pi x}{2l}, \quad (2)$$

where θ is the temperature at the plane x and at time t.

Σ' here signifies the sum of an infinite series in which the values of n in successive terms are the odd integers 1, 3, 5, etc. It is easy to verify that this solution satisfies all the required conditions.

If l is the maximum depth to which the θ_0 geotherm can possibly descend, then $\theta=\theta_0$ when $x=l$, and t is infinite. Substituting these values, we get

$$\theta_0=\frac{al^2}{2\kappa}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and if we use this equation to eliminate κ from (2), it becomes

$$\frac{\theta}{\theta_0}=\frac{x}{l}\left(2-\frac{x}{l}\right)+\frac{4}{\pi}\Sigma'\frac{1}{n}\left(1-\frac{8}{n^2\pi^2}\right)e^{-\frac{n^2\pi^2at}{8\theta_0}}\sin\frac{n\pi x}{2l}. \quad (4)$$

The following are the data adopted by Prof. Joly :—

Melting-point of basalt = 1150° C.
Heat developed per sec. per gram = $12{\cdot}64\times10^{-14}$ cal.
Density of basalt = 3·0, sp. heat = 0·267.
Conductivity of basalt = 0·004.

From these figures we get $\kappa=0{\cdot}005$ sq. cm. per sec., and $a=47{\cdot}3\times10^{-14}$ degree C. per sec.

Substituting in (3), we get $l=30{\cdot}6$ miles.

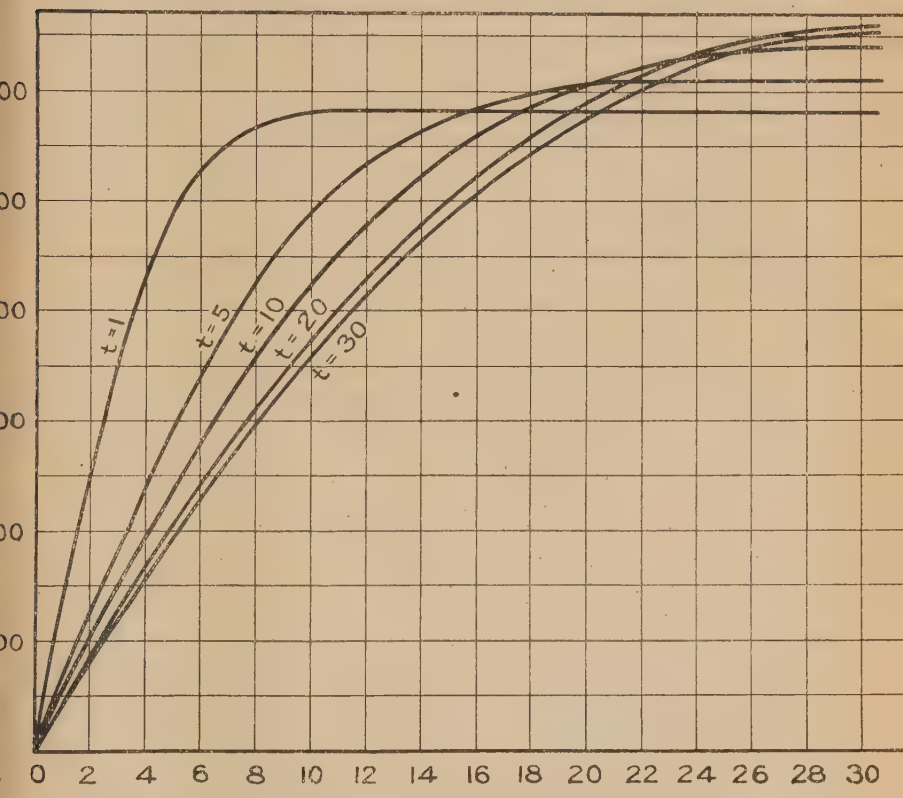
If, as will be convenient, we take one million years as our unit of time, then $a=14°{\cdot}9$ C. per million years. Using these values, the following figures for θ have been calculated from (4) :—

Temperature θ for different Times and Distances.

Time (millions of years).	Distance in miles from surface.					
	5·1	10·2	15·3	20·4	25·5	30·6
1	999°2	1160°9	1164°8	1164°9	1164°9	1164°9
5	611·6	999·9	1166·5	1214·3	1223·3	1224·4
10	492·0	864·8	1100·3	1222·5	1273·3	1286·2
15	444·7	799·5	1052·4	1210·5	1292·7	1317·6
20	421·2	764·5	1022·4	1196·5	1295·0	1326·5
25	408·1	743·9	1002·5	1183·2	1289·0	1323·8
30	400·0	730·6	988·0	1170·8	1279·6	1315·7

Since the rise of temperature in insulated material is 14°·9 in a million years, it will be seen that the last 15 miles lose no heat in the first million years. Actually, the calculation shows a very slight fall, affecting the second decimal place only.

I have traced the curves of temperature distribution for $t = 1$, 5, 10, 20, and 30 million years. The diagram would be confusing if more curves were included.



The position of the 1150° geotherm was derived from the curves and then calculated independently. The following results were obtained :—

Depth of the 1150° Geotherm at different Times.

Time (millions of years).	1.	5.	10.	15.	20.	25.	30.
Depth (miles)	8·6	14·5	17·0	18·1	18·8	19·3	19·6

The error introduced by omitting to treat the portion of the medium above 1150° as non-conducting does not become appreciable until a considerable thickness has been cooled below that temperature. This is evident from the flatness of the curves $t = 1$ and $t = 5$ at their upper parts. It is clear

that actually the heat generated in the lower regions would be held back, instead of being partly conducted away, so that the geotherms would advance somewhat farther than is indicated by the above calculations. We may conclude that in 30 million years the 1150° isotherm would descend to a depth of at least 20 miles. Again, if in equation (2) we put $l = 26{\cdot}2$ miles instead of 30·6, we find that in 30 million years the 1150° geotherm would just reach to 26·2 miles. Here no heat is held back, and as the escape of heat is facilitated by conferring on any part of the medium a greater conductivity than it actually possesses, this result constitutes a major limit to the distance. Thus in 30 million years the 1150° geotherm attains a depth which is greater than 19·6 miles and less than 26·2 miles.

XLIX. *On the Discontinuous Flow of Liquid past a Wedge of Small Angle. By* W. B. Morton, *M.A., Queen's University, Belfast* *.

Introduction and Summary.

THIS paper is in continuation of one published in the Philosophical Magazine of May 1921†, in which was treated the flow of liquid past a wedge of any angle. It was suggested to me by Mr. T. C. Tobin that it would be of interest to examine specially the case in which the angle of the wedge and the angle at which its face is met by the stream are both small, since this may be regarded as a rough approximation to what happens in the case of a screw-propeller. It seemed possible that the rather intractable analysis of the former paper might be capable of simplification by way of an approximate solution when the angles are small. I have not made much progress in this direction with motion of the most general type, when the backward part of the stream-line along the front face, passing the angle of the wedge, bends round and is caught by the back face, enclosing a pocket of dead water (see fig. 2 of the former paper). In the two limiting cases, however, designated by the names of Kirchhoff and Bobyleff, I have found some simplified results of a rather interesting kind. In the former the stream-line from the apex just grazes the edge of the back plane and in

* Communicated by the Author.

† Vol. xli. p. 801.

the latter it runs along its entire length, the stream dividing at the apex. When the angle of the wedge is small and the direction of the stream lies within it, the determining factor is found to be the ratio in which the wedge-angle is divided by the stream-direction. The actual magnitudes of the angles do not enter into the formulæ.

The following details are discussed :—

(1) The ratio of the breadths in the two limiting cases. Incidentally it is shown that the free stream-line round the upstream edge of a single plane approaches a definite form of curve as the angle of attack is decreased, while, of course, the scale of the curve decreases to zero.

(2) The ratio of the thrusts, in the Bobyleff case ; also, the loss of thrust brought about by the flow of the liquid along the rear plane when this extends so far as to bring the point of division of the stream to the corner.

(3) The manner in which the velocity of the liquid varies along the planes from zero, where the stream divides, to the full value at the edge where the free stream-line begins.

1. *The Ratio of the Breadths.*

It will be convenient to begin with a summary of the analysis of the case where an infinite stream divides at the apex of a wedge and flows along its faces. Bobyleff solved this for an equal-sided wedge and symmetrical impact. When the direction of the stream makes unequal angles with the faces their breadths must have a definite ratio, the broader plane being that which is met at the smaller angle. By flattening out the wedge we can get the case of a single lamina.

Let the angle of the wedge be $\gamma = \pi/n$, and let α and β be the parts into which it is divided by the direction of the stream. The configuration in the planes of

$$z = x + iy,$$

$$w = \phi + i\psi,$$

$$\Omega = \log\left(-\mathrm{Q}\frac{dz}{dw}\right),$$

$$= \log\frac{\mathrm{Q}}{q} + i\theta,$$

and the corresponding values of the auxiliary real variable u, are shown on fig. 1. Then

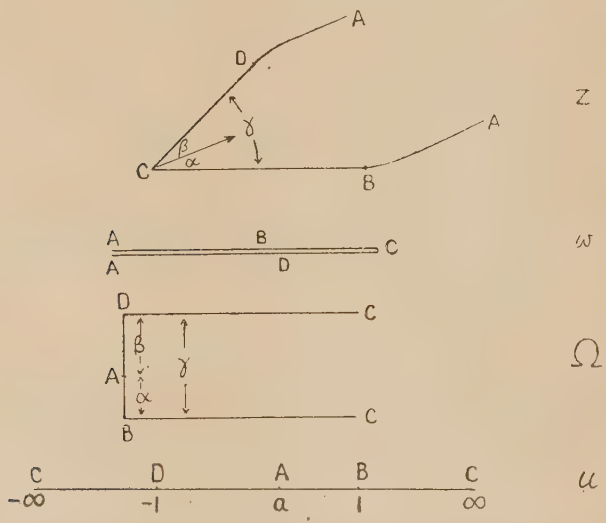
$$d\Omega/du = A(u^2-1)^{-\frac{1}{2}},$$

$$dw/du = B(u-a)^{-3}.$$

It is easily found that $A = 1/n$, and so

$$\Omega = \frac{1}{n}\log\{u+(u^2-1)^{\frac{1}{2}}\}.$$

Fig. 1.



Along the free stream-line, $u = \cos n\theta$ and in particular, for the point at infinity, $a = \cos n\alpha$.

$$dz/du = -B\{u+(u^2-1)^{\frac{1}{2}}\}^{\frac{1}{n}}/Q(u-a)^3.$$

For points on the faces of the wedge, where $|u|>1$, we obtain compact formulæ by introducing a new angular variable χ connected with u by the equation

$$u = (1+a\cos n\chi)/(a+\cos n\chi).$$

At the points C, B the values of χ are β and zero. The length of the face CB is found to be equal to

$$\frac{2Bn}{Q\sin^4 n\alpha}\int_0^{\beta} \sin^{1+\frac{1}{n}}\tfrac{1}{2}n(\beta+\chi)\,.\,\sin^{1-\frac{1}{n}}\tfrac{1}{2}n(\beta-\chi)\,.\,\sin n\chi\,.\,d\chi.$$

Now suppose n to become large. The angles $n\alpha, n\beta$ remain finite, being $\alpha\pi/\gamma, \beta\pi/\gamma$. The expression for the length CB reduces to $B/8Q \sin^4 \frac{1}{2}n\alpha$. CD is got by putting β for α. CB, CD may be called the α-side and the β side of the wedge. We have found that

$$\beta\text{-side}/\alpha\text{-side} = \sin^4 \tfrac{1}{2}n\alpha / \sin^4 \tfrac{1}{2}n\beta = \tan^4 \frac{\alpha}{\gamma}\frac{\pi}{2}.$$

This is the "Bobyleff ratio."

It is interesting to compare with the formula just obtained certain numerical results which have been worked out for me by Miss F. M. Chambers, M.Sc., using the exact formulæ and evaluating the integrals by planimeter. The values of γ can scarcely be regarded as "small," but the results are in satisfactory agreement.

γ.	α.	Ratio by Planimeter.	By Formula.
15°	5°	9	9
18	5	20·6	21·64
20	5	30·7	33·97
22½	5	52	56·98

To find the other limiting ratio we must consider the free stream-line from the upstream edge of a single plane and find where it is met by a second plane, set off in the dead water at angle γ with the first.

Making $n=1$ in the above analysis and putting $u=\cos\theta$ we easily find for the coordinates of a point on the stream-line referred to the upstream edge ($\theta=\pi$)

$$x = c\int_{\pi}^{\theta} \frac{\sin\theta\cos\theta\, d\theta}{(\cos\alpha - \cos\theta)^3},$$

$$y = c\int_{\pi}^{\theta} \frac{\sin^2\theta\, d\theta}{(\cos\alpha - \cos\theta)^3},$$

where c is written for the length B/Q.

As $\alpha \to 0$ the integrated values approach

$$x = \tfrac{1}{8}c\cot^2\tfrac{1}{2}\theta(\cot^2\tfrac{1}{2}\theta - 2),$$

$$y = \tfrac{1}{3}c\cot^3\tfrac{1}{2}\theta.$$

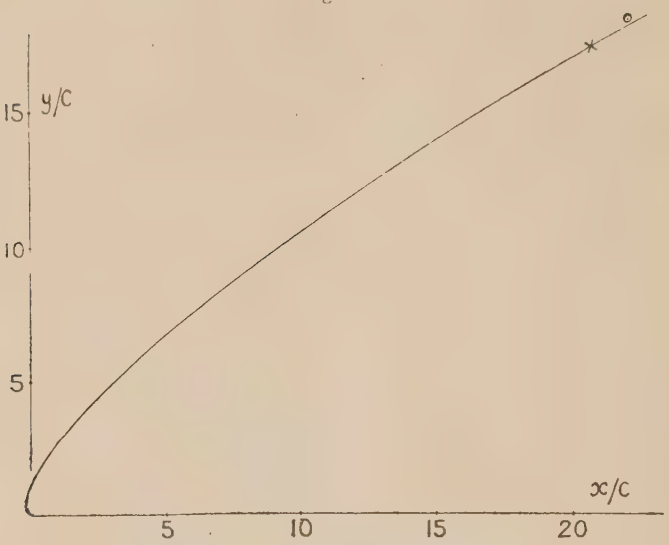
So that the equation to the limiting form for small angles of attack may be written

$$8x/c = \{1-(3y/c)^{2/3}\}^2 - 1.$$

The curve turns to the right at $\theta = \frac{1}{2}\pi$, $x = -\frac{1}{8}c$, $y = \frac{1}{3}c$, and crosses the y-axis again at $\theta = \cos^{-1}\frac{1}{3}$, $y = 2\sqrt{2}c/3$. Close to the edge it approximates to a semi-cubical parabola.

The curve is plotted on fig. 2. For comparison I have calculated some points on the exact curve for $\alpha = 5°$. Within the limits of the diagram the two curves are indistinguishable on this scale. The extreme points marked with a cross and a circle are the approximate and exact points for $\theta = 30°$.

Fig. 2.



At very distant points, as $\theta = 5°$ is approached, the divergence, of course, becomes great, as is seen from the following table of coordinates.

θ	Exact Curve.		Approximate Curve.	
	x.	y.	x.	y.
150°	−·017	·006	−·017	·006
120	−·070	·065	−·069	·064
90	−·126	·336	−·126	·333
60	·384	1·760	·375	1·732
30	22·087	18·295	20·767	17·331
10	3754·076	841·557	2100·9	497·76

Although this approximation gives a good idea of the form of the stream-line leaving the edge, it obviously cannot be used to obtain the intersection with a radius-vector making a small angle with the axis of x, for at the distant point where this meets the stream the angles α and θ are comparable in magnitude; we therefore go back to the exact

expressions for (xy) which, on integration, are found to be

$$\frac{x}{c} = \frac{2+\cos\alpha}{2(1+\cos\alpha)^2} + \frac{2\cos\theta - \cos\alpha}{2(\cos\alpha-\cos\theta)^2},$$

$$\frac{y}{c} = \frac{1}{2\sin^3\alpha}\left\{\frac{\sin\alpha\sin\theta\,(1-\cos\alpha\cos\theta)}{(\cos\alpha-\cos\theta)^2} - \log\frac{\sin\frac{1}{2}(\theta+\alpha)}{\sin\frac{1}{2}(\theta-\alpha)}\right\}.$$

Making θ, α small and retaining only the terms of the largest order,

$$\frac{x}{c} = \frac{2}{(\theta^2-\alpha^2)^2},$$

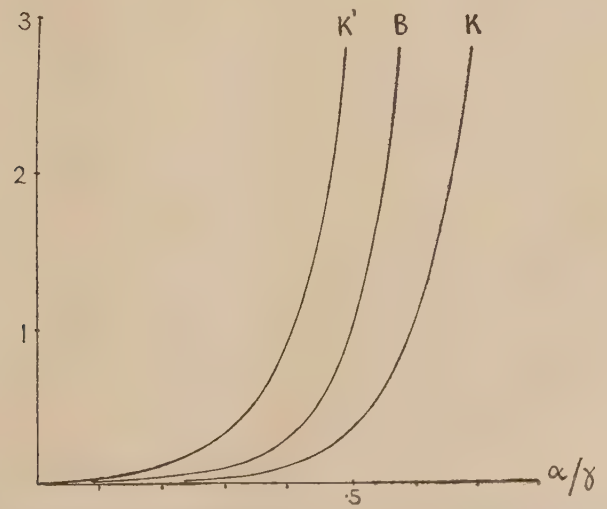
$$\frac{y}{c} = \frac{1}{2\alpha^3}\left\{\frac{2\alpha\theta(\theta^2+\alpha^2)}{(\theta^2-\alpha^2)^2} - \log\frac{\theta+\alpha}{\theta-\alpha}\right\}.$$

At the point where the second plane reaches the stream-line $y=\gamma x$. So

$$\frac{\gamma}{\alpha} = \frac{\theta(\theta^2+\alpha^2)}{2\alpha^3} - \frac{(\theta^2-\alpha^2)^2}{4\alpha^4}\log\frac{\theta+\alpha}{\theta-\alpha}.$$

The breadth of the first plane is $c(\pi\sin\alpha+4)/2\sin^4\alpha$, which may be put $=2c/\alpha^4$. The required approximate ratio is then x/breadth of plane $=\alpha^4/(\theta^2-\alpha^2)^2$. Thus assuming a value

Fig. 3.



for θ/α (being >1) we can find the corresponding associated values of α/γ and of the breadth ratio, which can then be plotted together.

On fig. 3 the curves marked B and K show the Bobyleff

and Kirchhoff ratios for different values of α/γ. They may be compared with the corresponding and similar curves given in the previous paper for a right-angled wedge. The curve marked K′ shows, over any value of α/γ, the reciprocal of the K-ratio for $1-\alpha/\gamma$ or β/γ.

As an illustration of the information contained in this diagram suppose a wedge-shaped blade to be met by a stream at an angle of 5°. Take the breadth of the front face of the blade as unity and suppose a back face making an angle of 15° with the front one, to be extended to an increasing breadth. Then, over the value $\alpha/\gamma=\frac{1}{3}$, three critical breadths are indicated, separating four distinct types of motion :

(1) While the back face lies altogether in the dead-water region, the stream divides very near the edge on the front face. Calculation for $\alpha=5°$ shows that the distance from the edge to the point of division is less than 1/50,000 of the breadth of the plane. When the back plane reaches a breadth of about ·05 (on the curve K), it interferes with the stream-line.

(2) After this a small pocket of dead water is formed at the edge, on the back plane, beyond which the stream-line runs along the remaining distance of this plane to its further edge. The point of stream-division comes still nearer to the edge on the front plane. There is, of course, a loss of thrust. When the breadth of the back plane reaches about ·11 we are on the B-curve. The stream divides at the angle of the wedge. In the next part of the work we shall find an approximate value for the loss of thrust at this stage.

(3) The point of division of the stream now comes on the back face, and a pocket of dead water is formed on the front face at the edge. With further extension of the rear plane this pocket spreads until, on the curve K′, for breadth of about ·45, it covers the whole of the front face. At some point in this stage the resultant thrust vanishes and then reverses.

(4) With further extension we get the original motion with the rôles of the planes reversed and an incidence on the other face at an angle 10°.

By following a horizontal instead of a vertical line across the diagram the effect of changing the angle of incidence can be followed in a similar manner.

Without claiming for this investigation any direct application to practical conditions, one may, perhaps, infer from it that with small angles of attack the nature of the motion and the magnitude of the thrust obtained will be sensitive to comparatively small changes in the geometrical configuration.

As a test of the closeness of the Kirchhoff approximation I have calculated the coordinates of the point $\theta=10^\circ$ on the accurate stream-line for $\alpha=5^\circ$. I find that the radius vector makes an angle of $12^\circ\,38'$ with the plane and that its length is ·104 of the breadth of the plane. The value of α/γ is ·396 and the height of the K-curve for this abscissa is about ·11.

2. *Thrusts on the Planes.*

At a point on the plane CB we have the velocity

$$q=Q\{u+(u^2-1)^{\frac{1}{2}}\}^{-\frac{1}{n}},$$

or, in terms of the angle χ already used,

$$q=Q\sin^{-\frac{1}{n}}\tfrac{1}{2}n(\beta+\chi)\,.\,\sin^{\frac{1}{n}}\tfrac{1}{2}n(\beta-\chi).$$

The excess pressure

$$\begin{aligned}p&=\tfrac{1}{2}\rho(Q^2-q^2)\\&=\tfrac{1}{2}Q^2\rho\left\{1-\sin^{-\frac{2}{n}}\tfrac{1}{2}n(\beta+\chi)\,.\,\sin^{\frac{2}{n}}\tfrac{1}{2}n(\beta-\chi)\right\}.\end{aligned}$$

Multiplying by the element of length and integrating along the plane, we obtain for the thrust on CB

$$\frac{BQ\rho n}{\sin^4 n\alpha}\int_0^\beta\Big\{\sin^{1+\frac{1}{n}}\tfrac{1}{2}n(\beta+\chi)\,.\,\sin^{1-\frac{1}{n}}\tfrac{1}{2}n(\beta-\chi)$$
$$-\sin^{1-\frac{1}{n}}\tfrac{1}{2}n(\beta+\chi)\sin^{1+\frac{1}{n}}\tfrac{1}{2}n(\beta-\chi)\Big\}\sin n\chi d\chi.$$

When n becomes large the expression for p approaches the value

$$\tfrac{1}{2}Q^2\rho\,.\,\frac{2}{n}\log\frac{\sin\frac{1}{2}n(\beta+\chi)}{\sin\frac{1}{2}n(\beta-\chi)},$$

and the approximate value of the thrust is

$$\frac{2BQ\rho}{\sin^4 n\alpha}\int_0^\beta\sin\tfrac{1}{2}n(\beta+\chi)\,.\,\sin\tfrac{1}{2}n(\beta-\chi)\,.\,\sin n\chi$$
$$\times\log\frac{\sin\frac{1}{2}n(\beta+\chi)}{\sin\frac{1}{2}n(\beta-\chi)}\,.\,d\chi.$$

This can be integrated by parts; the result is

$$\Big[\tfrac{1}{4}\sin n\beta(\sin n\chi-n\chi\cos n\beta)$$
$$-\tfrac{1}{4}(\cos n\chi-\cos n\beta)^2\log\frac{\sin\frac{1}{2}n(\beta+\chi)}{\sin\frac{1}{2}n(\beta-\chi)}\Big]_0^\beta,$$

omitting the factor $2BQ\rho/n\sin^4 n\alpha$.

The logarithmic term vanishes at both limits, and we obtain for the thrust

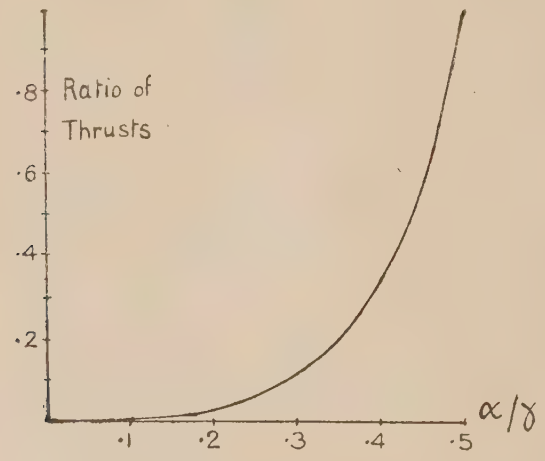
$$BQ\rho(\sin n\beta - n\beta \,.\, \cos n\beta)/2n \sin^3 n\alpha.$$

It follows that thrust on α-side : thrust on β-side

$$= \left(1-\frac{\beta}{\gamma}\pi \cot\frac{\beta}{\gamma}\pi\right) : \left(1-\frac{\alpha}{\gamma}\pi \cot\frac{\alpha}{\gamma}\pi\right).$$

The graph of this ratio is shown on fig. 4. I add a table

Fig. 4.



giving the values found by planimeter for the four cases referred to in the preceding paragraph, along with those given by the approximate formula. In the first of these the areas were too small to give an accurate measurement.

γ.	α.	Ratio by Planimeter.	By Formula.
15°	5°	6·8	5·58
18	5	12·9	12·67
20	5	13·2	13·64
22½	5	27·9	22·3

If now the two faces are taken together, the resultant thrust on the wedge, when the angle is small, may be taken as the

difference of the thrusts on the two faces. Its magnitude is

$$BQ\rho\gamma \cos n\alpha/2 \sin^3 n\alpha.$$

Dividing by the breadth of the front face, which is $B/8Q \sin^4 n\alpha$, we get for the thrust per unit breadth the expression

$$Q^2\rho\gamma \sin \tfrac{1}{2}n\alpha \,.\, \cos n\alpha/2 \cos^3 \tfrac{1}{2}n\alpha.$$

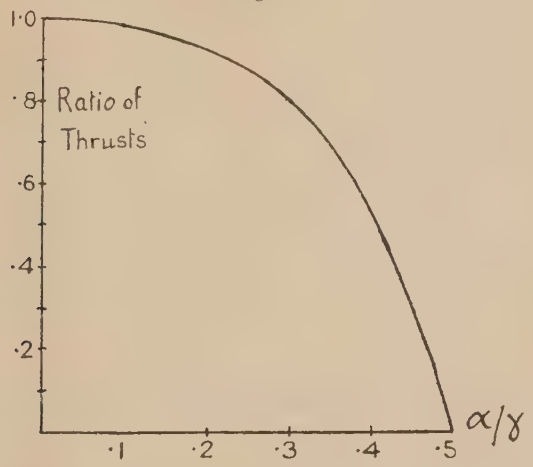
If the back plane were absent the thrust per unit breadth would be $\frac{1}{4}Q^2\rho\pi\alpha$ and so the effect of the back plane, at this particular breadth, is to reduce the thrust by the factor

$$\sin \tfrac{1}{2}n\alpha \,.\, \cos n\alpha/\tfrac{1}{2}n\alpha \,.\, \cos^3 \tfrac{1}{2}n\alpha$$

$$(n\alpha = \frac{\alpha}{\gamma} \,.\, \pi).$$

This function is plotted against α/γ on fig. 5.

Fig. 5.



Returning to fig. 3 we see that the above work has given the decrease in the effective thrust brought about as the breadth of the second plane increases from k, when it first interferes with the motion of the liquid, to b when the streamline divides at the apex, k b k' being used forthe ordinates of the three curves. The negative thrust for breadth k' is also known ; its ratio to the original thrust on the single plane is evidently $k'\beta/\alpha$. With these data it is further possible to get a rough estimate of the breadth of the second plane

which makes the resultant thrust vanish, if we make the assumption that the decrease of thrust is connected by an approximately linear relation with the increase of breadth of the second plane. This procedure would be suggested if the proportionality between decrease of thrust and increase of breadth were found to hold between the critical cases which have been discussed. This is exactly the case when the direction of the stream bisects the angle of the wedge, for then we have

thrust 1 for breadth k,
„ 0 „ 1,
„ $-k'$ „ k'.

Readings taken from figs. 3 and 5 show that the relation holds approximately for other values of α/γ which are not too small to permit of accurate readings. It is otherwise evident that a graph for this fourth critical value of the breadth, lying between B and K′, is roughly determined by the conditions of touching the axis at the origin and passing through the point (0·5, 1).

3. *Variation of Velocity along the Planes.*

Comparatively simple relations between the velocity of the liquid and the distance, measured from the point of zero velocity, can be found in certain cases, and from these the distribution of thrust over the planes.

Using the angle χ as before and considering the plane CB in the general Bobyleff case, we have for the distance of a point from the apex

$$x = A\int_{\chi}^{\beta} \sin^{1+\frac{1}{n}} \tfrac{1}{2}n(\beta+\chi) \cdot \sin^{1-\frac{1}{n}} \tfrac{1}{2}n(\beta-\chi) \cdot \sin n\chi \cdot d\chi,$$

with

$$q = \sin \tfrac{1}{2}n(\beta+\chi)/\sin \tfrac{1}{2}n(\beta-\chi).$$

The constant A will be given such a value as will make $x=1$ along with $q=1$ at the edge where $\chi=0$ and the free streamline begins.

The integral for x can be evaluated in two cases,

(a) when the wedge flattens out to a plane,

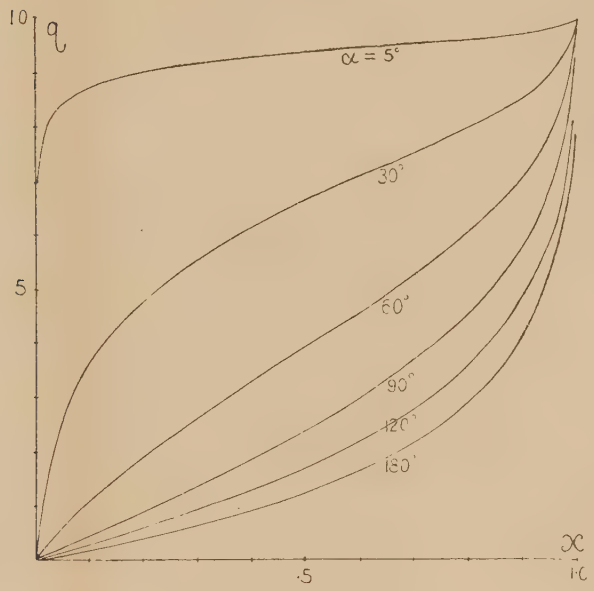
(b) when, as in the previous work, n is large.

(a). Replacing β by $(\pi-\alpha)$ the expression for x becomes

$$A\{2(\cos\chi+\cos\alpha)+\sin(\chi+\alpha)\,.\,\sin(2\alpha-\chi) \\ -(\pi-\alpha-\chi)\sin\alpha\}.$$

The result of plotting q against x for different angles of incidence is shown on fig. 6.

Fig. 6.



A curious feature of these curves is seen in the approach to a limiting form as the angle α approaches π, *i. e.* on the short upstream side in the case of very oblique incidence. The equation to this limiting graph is found by replacing χ by $(\pi-\chi)$ in the above, and expanding in powers of the small angles $\chi\alpha$. The lowest order which does not vanish is the fourth. The result is

$$x=(\alpha-\chi)(17\alpha^3+17\alpha^2\chi+11\alpha\chi^2+3\chi^3)/17\alpha^4,$$

making $x=1$ when $\chi=0$. Along with this

$$q=(\alpha-\chi)/(\alpha+\chi).$$

Elimination of χ/α gives the algebraic equation

$$x = 16q(q^3+4q^2+6q+6)/17(1+q)^4.$$

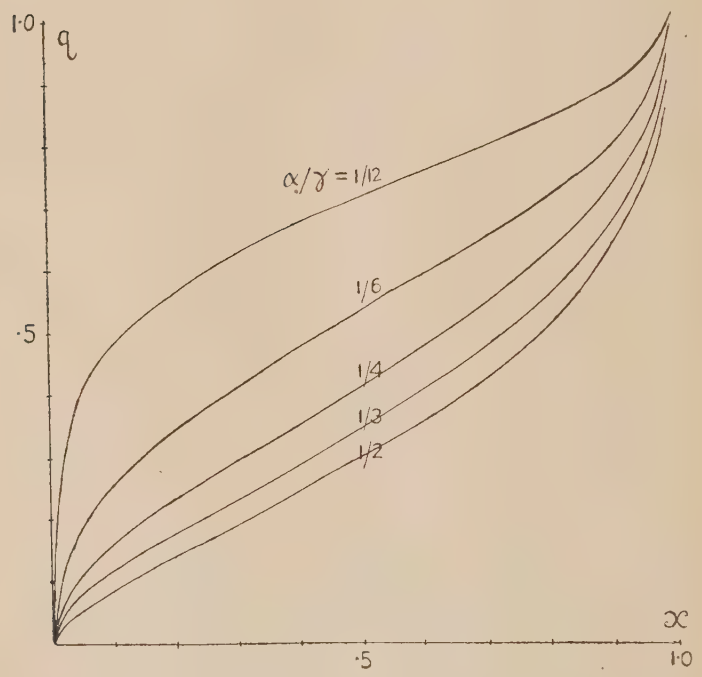
(*b*). By means of the approximations already used we obtain

$$x = (\cos n\chi - \cos n\beta)^2/(1-\cos n\beta)^2.$$

It is now easy to eliminate χ and connect xq directly. The result is

$$x = \left\{ 4q \sin^2 \frac{\alpha}{\gamma}\frac{\pi}{2} \Big/ (1-2q\cos\frac{\alpha}{\gamma}\pi+q^2) \right\}^2.$$

Fig. 7.



The graphs are shown on fig. 7. They agree closely with results obtained by planimeter in the special cases already referred to.

L. *The Crystal Structures of the Rhombohedral Forms of Selenium and Tellurium.*

By A. J. Bradley, *M.Sc., Research Student in Physics, The Physical Laboratories, University of Manchester* *.

[Plate X.]

A. Selenium.

1. *Introductory.*

ACCORDING to Groth †, selenium crystallizes in three modifications, of which two belong to the monoclinic system, and the third to the rhombohedral system. The last form, known as metallic selenium, is isomorphous with the naturally occurring crystals of tellurium. It has a specific gravity of about 4·8 ‡, and crystallizes in small hexagonal prisms. There is no record of crystals being obtained sufficiently good to give any definite value for the interfacial angles and the axial ratio. F. C. Brown § describes the production of crystals of metallic selenium of three distinct types by distillation at various temperatures and under varying partial pressures of selenium vapour. The first type were rhombohedral or hexagonal in shape, and agreed with Muthmann's description. Other crystals grew in clusters of spines or needles. These acicular crystals were quite stiff and tough, in striking contrast with the third type, which consisted of flexible sheets, the thickness being of the order of 0·01 mm. These lamellar crystals were produced when the temperature was low.

2. *Experimental.*

The crystal structure was investigated by the method of the powder photograph. The experimental arrangements were exactly the same as in the case of arsenic ‖. The first photographs obtained were from the finely-divided grey selenium, the particles of which were too small to show any lustre. Not many lines were visible, and these were weak, broad, and indistinct. There was very much general blackening of the film, which indicates the presence of a large proportion of amorphous material. Only approximate

* Communicated by Prof. W. L. Bragg, F.R.S.

† *Chemische Krystallographie*, i. p. 33 (1906).

‡ Muthmann, *Zeitschr. f. Krystall.* xvii. p. 354 (1890).

§ Phys. Rev. (2) iv. p. 85 (1914).

‖ A. J. Bradley Phil. Mag. xlvii. p. 657 (1924)

measurements could be made, but these were sufficient to indicate the nature of the space-lattice. By comparing the observed spacings with those given by Hull's * graph for a simple triangular lattice, an agreement was found for an axial ratio of about 1·14. Density considerations show that each point of the lattice represents three atoms of selenium. No further progress could be made in the elucidation of these films, so an attempt was made to grow some larger crystals of selenium, and in this way to obtain a mass of material free from amorphous diluents.

The crude vitreous selenium was placed in a glass cylindrical vessel which was carefully evacuated, and the selenium was heated by placing the cylinder vertically with the lower end in an electrically-heated jacket. After several days crystals appeared in the cooler portion of the vessel. The sublimate formed three well-marked zones. First, nearest the heated end, was a sharply-defined narrow horizontal zone of definitely crystalline material, which ultimately grew almost across the tube. Then followed a broad band of shiny grey scales covering the walls of the vessel, which gradually gave way to a still broader zone consisting of an attenuated red film.

The crystals were of the lamellar type, about a centimetre long and about 0·4 mm. across. In general appearance they resembled the crystals described by Brown (*loc. cit.*). No other form of crystal was observed.

A sample of these lamellar crystals was ground in an agate mortar and exposed to X-rays in the usual manner. The photograph so obtained was identical with the earlier films in respect to the positions of the lines, but the intensities were not all in the same relative order in the two sets of films. The most obvious explanation of this difference is to be found in the large size of the crystalline particles in the second experiment. In order to test this hypothesis, two more exposures were made with more carefully-ground specimens of the recrystallized selenium. A comparison of the intensities showed that in both cases the lines were in almost the same order of intensity as those on the film taken with the crude material, though one or two lines showed a tendency to deviate towards the order given by the coarsely-ground specimen. The orders of intensity are given in Table I. They were obtained by the method already described in the case of arsenic (*loc. cit.*). Column IV. refers to a film taken with the crude material; Column V.

* A. W. Hull, Phys. Rev. (2) xvii. p. 571 (1921).

was obtained from the coarse crystals; and Columns VI. and VII. from the more finely-ground specimen.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.
			Order of Intensity.			
$\frac{d}{n}$(Obs.) $\times 10^{-8}$ cm.	$\frac{d}{n}$(Calc.) $\times 10^{-8}$ cm.	Reflecting Planes.	Powder.	Large crystals.	Small crystals.	
...	4·96	0001	...	...	...	...
3·71	3·77	10$\bar{1}$0	3	2	3	4
2·982	2·999	10$\bar{1}$1	1	1	1	1
...	2·480	0002	...	...	...	...
2·174	2·175	11$\bar{2}$0	...	6	6	9
2·070	2·071	10$\bar{1}$2	2	3	2	2
1·998	1·990	11$\bar{2}$1				
1·891	1·883	20$\bar{2}$0	...	16	18	18
1·761	1·762	20$\bar{2}$1	4	4	4	3
1·639	1·653	0003	5	10	7	5
	1·634	11$\bar{2}$2				
1·502	1·511	10$\bar{1}$3	6	10	7	5
	1·499	20$\bar{2}$2				
1·430	1·423	12$\bar{3}$0	8	5	5	5
1·371	1·370	12$\bar{3}$1	...	12	12	14
1·315	1·315	11$\bar{2}$3	...	15	13	12
1·271	1·256	30$\bar{3}$0	...	19	19	19
1·241	1·241	20$\bar{2}$3	..	9	10	10
	1·240	0004				
	1·234	12$\bar{3}$2				
1·220	1·217	3031				
1·177	1·176	10$\bar{1}$4	...	15	15	15
1·122	1·119	30$\bar{3}$2	...	14	13	13
1·079	1·087	22$\bar{4}$0	7	7	9	8
	1·077	12$\bar{3}$3				
	1·075	11$\bar{2}$4				
1·061	1·063	22$\bar{4}$1				
1·043	1·045	1340	..	20	20	20
1·025	1·034	20$\bar{2}$4	...	8	11	11
	1·022	13$\bar{4}$1				
·997	·999	22$\bar{4}$2	...	17	17	17
	·995	30$\bar{3}$3				
·963	·963	13$\bar{4}$2	...	17	16	16
	·957	10$\bar{1}$5				

It appears from a comparison of the photographs obtained with the coarse and finely-divided material, that in the former case there is a tendency for planes which make small angles with the trigonal axis to give too great a relative intensity of reflexion. Thus in Column V., lines belonging to planes (1010), (2020), (11$\bar{2}$0) are all too strong, whereas

those corresponding to planes (0003), (11$\bar{2}$2), (10$\bar{1}$3), (20$\bar{2}$2) are all too weak. This is probably due to the lamellar nature of the crystals, which favours a definite orientation.

3. *Selection of a possible Structure for Selenium.*

The film whose order of intensity is given in Column VII. was the clearest obtained, and hence measurements from this film were used to find the lattice dimensions. The calculations were similar to those for arsenic (*loc. cit.*), and Column I. gives the values of $\frac{d}{n}$ obtained in this way. Every line which appeared on the first photographs with the crude material is repeated on this film, but in addition many lines which were there too faint to show up, now appear. Only those spacings are present which fit on Hull's graph for a triangular lattice of axial ratio $c:a=1{\cdot}14:1$. Two important lines, however, are still missing. This omission affords a valuable clue to the structure, as will be seen later.

From Hull's graph we can also obtain the indices of the planes corresponding to each line on the film. Thus the spacing $\frac{d}{n}=1{\cdot}89$ Å. corresponds to the plane (20$\bar{2}$0). The spacing of (10$\bar{1}$0) planes is therefore 3·78 Å. This value is chosen in preference to that obtained from the first-order reflexion on account of the much greater sharpness of the lines (20$\bar{2}$0). The volume of the unit cell, which is a right rhombic prism and contains one point of the lattice, is $\frac{4}{3}d^3_{10\bar{1}0}\times 1{\cdot}14=82{\cdot}0\times 10^{-24}$ c.c., where $d_{10\bar{1}0}$ is the spacing of planes (10$\bar{1}$0). Assuming the density of selenium to be 4·8 and its atomic weight 79·2, and taking the weight of the hydrogen atom as $1{\cdot}663\times 10^{-24}$ gm. and its atomic weight as 1·008, the volume occupied by one atom of selenium is $27{\cdot}24\times 10^{-24}$ c.c. The number of atoms associated with each point of the lattice is therefore $\frac{82{\cdot}4}{27{\cdot}24}=3{\cdot}01$. In other words, the structure consists of three interpenetrating lattices.

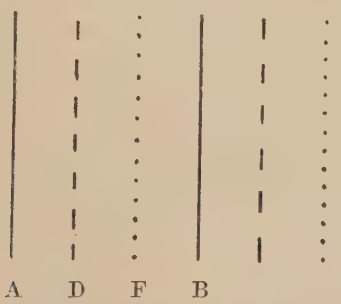
Every value of $\frac{d}{n}$ within a certain range was then calculated for such a system and for the constants given above. These values agreed with the observed values of Column I., but were on the whole 0·1 per cent. too high. After correcting for this difference, the calculated values are

given in Column II. From these corrected values we obtain the length of the side of the base of a unit cell, $a=4{\cdot}35$ Å. This confirms the results obtained by Miss M. K. Slattery *, who found that the structure of selenium consisted of a simple triangular lattice of axial ratio 1·14 and length of side of base 4·34 Å, three atoms being associated with each point of the lattice. The corrected density will be 4·82.

It is interesting to compare these results with the observations of F. C. Brown † on the lamellar crystals of selenium. Brown considered that these crystals belonged to the monoclinic system, axial ratio $a:b:c=1{\cdot}0:0{\cdot}18:6{\cdot}0$; $\beta=60°$. As the ratio $c:a$ is an integer and the angle β is 60°, it seems likely that the crystals are really trigonal. All the X-ray data fit in with this assumption, and measurements of lamellar crystals which I have made point to the same conclusion. The crystals appear to be composite, consisting of a number of parallel growths. In one case a single crystal of measurable dimensions was isolated from a lamellar crystal, which possessed clearly-defined trigonal symmetry. It gave values for the interfacial angles $(10\bar{1}1):(1\bar{1}01)$, $rr=87°\ 36'$, corresponding to an axial ratio $c:a=1{\cdot}15$. It does not seem likely that there is any difference in structure between Brown's three forms of selenium, especially in view of his own observations on the identity of the electrical, light electric, and electromechanical properties of selenium crystals of the three forms.

It remains to discover the mutual orientation of the three lattices which compose the selenium structure. All the

Fig. 1.



spacings tabulated in Column II. have their counterpart in Column I. except (0001) and (0002). The spacing (0001) of a single lattice (AB in fig. 1) must therefore be divided

* Phys. Rev. (2) xxi. p. 378 (1923).

† Phys. Rev. (2) v. p. 236 (1915).

by the planes D and F belonging to the other lattices, so that AD = DF = FB ; the first reflexion will correspond to AD, the (0003) spacing.

Further elucidation of the structure depends upon considerations of symmetry. Assuming the crystals to be trigonal, their structure must constitute a Sohncke * point system †. There are only eight such systems possessing trigonal symmetry, in which the spacing (0001) is divided by three. Hexagonal point systems can be ruled out, as they require at least six atoms to each point of the triangular lattice. Five of these trigonal systems possess $2-al$ axes of symmetry, namely:—

1. Nos. 19 and 20.—Right and Left compound 3-point screw systems.
2. No. 22.—Compound Rhombohedron system.
3. Nos. 23 and 24.—Right and Left alternating 3-point screw systems.

   Systems 19 and 23 are the mirror images of systems 20 and 24 respectively, the screws being in one case right-handed and in the other left-handed.

In point systems Nos. 19, 20, 23, and 24 there are in general six points grouped in pairs round each point of the simple triangular lattice ; the pairs are symmetrical about the three $2-al$ axes. In the present case we have only three atoms to each lattice point, so that in place of three pairs of points, there is a single point on each of the three $2-al$ axes. System 22 has in general eighteen atoms to each lattice point. If we simplify this by reducing the number of atoms to three, the structure becomes a simple rhombohedral lattice. Such an arrangement is impossible for selenium, as reflexions from many of the wider spacings which actually occur could not then be given.

The conditions for systems 19, 20, 23, 24 are completely satisfied by the observed spacings.

Fig. 2 gives a projection of systems 19 and 20, and fig. 3 of systems 23 and 24, the trigonal axes being perpendicular to the plane of the paper. Differently shaded circles represent atoms at different levels along the trigonal axes.

* Sohncke, *Entwickelung einer Theorie der Kristallstruktur*, 1871.

† If not, the structure would possess operations of the second sort, and the atoms would occur in pairs, which is not the case.

Fig. 2.

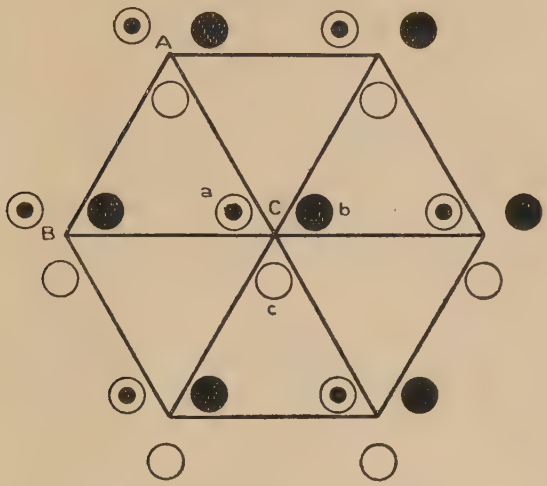
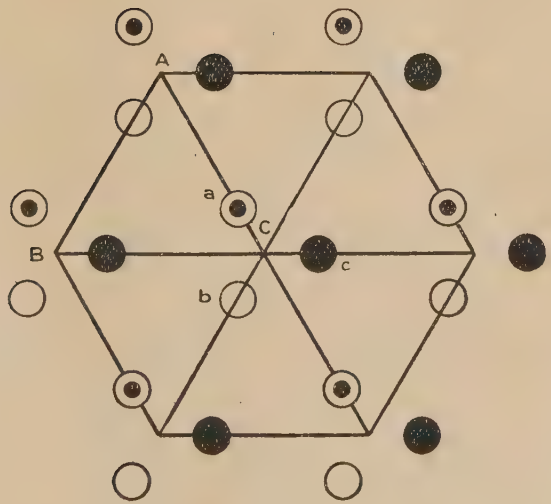


Fig. 3.



Each of these systems has an infinite number of parallel 3—*al* screw axes, and also an infinite number of non-intersecting 2—*al* axes, lying in planes perpendicular to the

3—*al* axes. Figs. 4 and 5 show the positions of the axes in systems 19 and 20, and 23 and 24 respectively. The 2—*al*

Fig. 4.

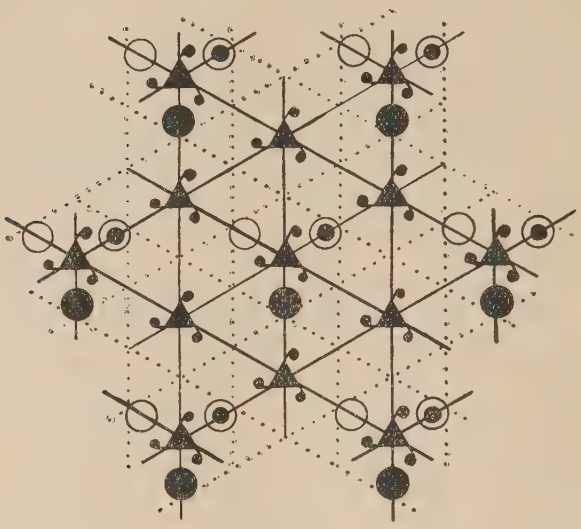
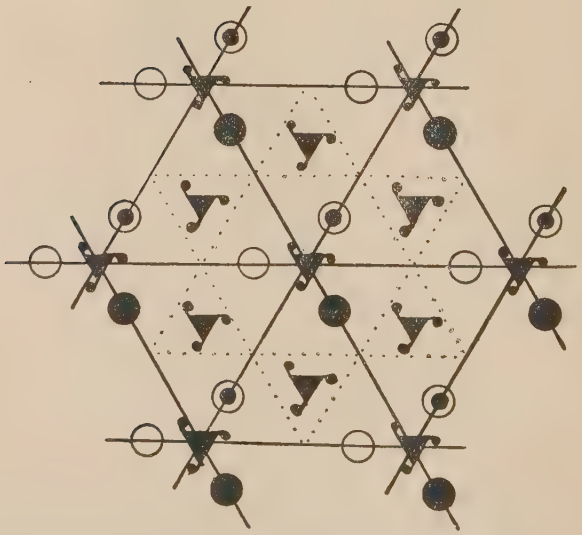


Fig. 5.



axes are of two kinds—rotatory (indicated by continuous lines) and screw (indicated by dotted lines). The arrangement of the axes in fig. 4 shows that the structure belongs

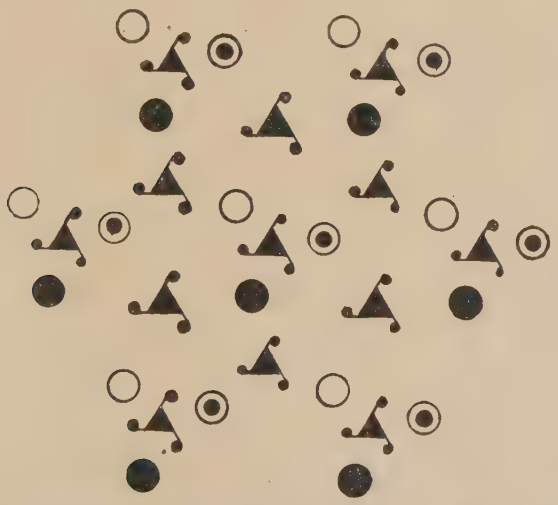
to the general space group * D_3^3 or D_3^5, and that shown in fig. 5 to the space group D_3^4 or D_3^6. Both are isomorphous with the point group D_3, so that if selenium possesses either of these two types of structure, its symmetry will be trigonal holoaxial.

In each case there is a variable parameter—the ratio of the size of the small triangle *abc* to that of the large triangle ABC (figs. 2 and 3). Upon the value of this parameter depends the intensity of reflexion from all planes except (0001) for all orders of reflexion. It is therefore possible to test the validity of either of these structures by attempting to find a value for the variable parameter, which will give the observed intensities of reflexion. If such a value does not exist, the structure must be of another type.

Of the systems which are without $2-al$ axes, No. 18 can be ruled out immediately for similar reasons to those used for No. 22. There remain :—

Nos. 15 and 16.—Right and left three-point screw systems.

Fig. 6.



These systems differ only from the four just considered in that the sides of the small triangle *abc* are now neither parallel nor perpendicular to the sides of the large triangle ABC. Fig. 6 shows a projection perpendicular to the trigonal axes of a possible structure belonging to this system. It is a space group C_3^2 or C_3^3, and possesses only $3-al$ screw axes and no other elements of symmetry. It is isomorphous with the point group C_3, so that the crystal

* Hilton, 'Mathematical Crystallography,' p. 222 (1903).

symmetry would be trigonal polar. As far as evidence from the crystal form can show, there is no reason for assigning the crystals to a class with such low symmetry; the other types of structure therefore seem preferable.

It can readily be shown that a structure based on systems 19 and 20 will not fit in with the experimental results. The observed orders of intensity of reflexion are given in Table II., Column III., and are the mean of the values in

TABLE II.

I. Reflecting Planes.	II. $\frac{N}{\sin^2\theta}$.	III. Observed Order of Intensity.	IV. Calculated Order of Intensity. B=0.	V. B=3·4.	VI. Calculated Equation (3).	VII. Intensity Equation (4).
0001	...	...	...	...	...	...
$10\bar{1}0$	140·0	3	8	3	24·2	23·9
$10\bar{1}1$	180·1	1	1	1	51·0	49·5
0002	...	...	...	...	...	...
$11\bar{2}0$	47·8	9	12	9	8·21	8·00
$10\bar{1}2$	86·6	2	2	2	19·1	18·4
$11\bar{2}1$	80·9				15·3	14·8
2020	36·2	18	18	17	1·48	1·42
2021	62·8	4	7	4	13·5	13·0
0003	9·05	5	9	5	3·80	3·65
$11\bar{2}2$	54·3				8·0	7·70
$10\bar{1}3$	45·8	6	4	6	3·74	3·55
2022	45·8				7·75	7·38
$12\bar{3}0$	41·5	6	5	7	10·05	9·40
$12\bar{3}1$	76·2	13	16	12	3·27	3·09
$11\bar{2}3$	36·2	12	14	13	2·90	2·82
$30\bar{3}0$	16·4	19	20	20	·02	·02
0004	...	...	...	...	...	...
$20\bar{2}3$	31·3	10	10	10	·61	·58
$12\bar{3}2$	62·6				2·15	2·01
$30\bar{3}1$	30·1				3·50	3·27
1014	28·0	15	15	16	2·30	2·15
3032	25·6	13	13	15	2·33	2·18
$22\bar{4}0$	11·8	8	3	8	·79	·75
$12\bar{3}3$	47·2				5·50	5·18
$11\bar{2}4$	23·6				1·33	1·26
2241	22·8				1·00	·94
$13\bar{4}0$	22·1	20	19	19	·31	·30
$20\bar{2}4$	21·3	11	6	11	1·28	1·25
$13\bar{4}1$	42·6				2·49	2·43
2242	20·1	17	17	18	·66	·68
$30\bar{3}3$	20·1				·01	·01
$13\bar{4}2$	39·5	16	11	14	1·99	2·08
$10\bar{1}5$	19·76				·86	·90
	Total error		41	10		

Table I., Columns IV., VI., and VII. If x is the ratio of ab to AB (fig. 2) it can be shown that for planes $(h0h0)$, the phase factor is given by $F = 5 + 4\cos 2\pi xh$. As the glancing angle increases, the observed reflexions for different orders fall away more quickly than they would normally do, judging from other lines on the film; hence

$$F_{10\bar{1}0} > F_{20\bar{2}0} > F_{30\bar{3}0} \cdot 2\pi x < 80°.$$

For planes $(h0\bar{h}l)$ where l is not a multiple of 3, $F = 2 - 2\cos 2\pi xh$. After allowing for the difference in the number of co-operating planes, a comparison of neighbouring lines on the film shows :—

1. $(10\bar{1}1)$ is greater than $(10\bar{1}0)$; $2\pi x > 120°$.
2. $(20\bar{2}1)$ is much greater than $(20\bar{2}0)$; $2\pi x$ lies between 60° and 120°.
3. $(10\bar{1}4)$ and $(30\bar{3}2)$ are almost equal ; $2\pi x = 90°$ or 180°. $2\pi x \nless 80°$.
4. $(30\bar{3}0) < (10\bar{1}4)$ or $(30\bar{3}2)$; $2\pi x$ lies between 45° and 80°, or between 160° and 180°.

Only values of $2\pi x$ between 0 and 180° have been considered, as all possible values of F occur within those limits. It is clear that no value of x can satisfy these conditions even approximately, so systems 19 and 20 can be definitely rejected. Only systems 23 and 24 remain.

4. *Confirmation of the Structure and Evaluation of the Indeterminate Parameter.*

In systems 23 and 24 the atoms are arranged as follows:—

m, n, p ;	$m+2x, n+x, p+\frac{1}{3}$;	$m+x, n-x, p+\frac{2}{3}$
$m+1, n, p$;	$m+2x+1, n+x, p+\frac{1}{3}$;	$m+x+1, n-x, p+\frac{2}{3}$
$m, n+1, p$;	$m+2x, n+x+1, p+\frac{1}{3}$;	$m+x, n-x+1, p+\frac{2}{3}$

where m, n, p are integers and x is the ratio of the distance aC to AC (fig. 3). The axes of reference are two axis at 120° to each other and at 90° to the third axis. The phase factor for planes (hkl) * will therefore be given by :—

$$F_{hkl} = 3 + 2\{\cos(2xh + xk + \tfrac{1}{3}l)2\pi + \cos(xh - xk + \tfrac{2}{3}l)2\pi + \cos(xh + 2xk - \tfrac{1}{3}l)2\pi\} \quad . \quad . \quad (1)$$

The phase factors for all planes giving observed reflexions

* I. e. $(h\,k\,i\,l)$. The index i being dependent on h and k is redundant for any calculations.

were tabulated for various values of x and plotted graphically for reference. Planes $(h0\bar{h}l)$, where l is not a multiple of 3, give two different values for the phase factor, depending on the signs of h and l. There are an equal number of planes giving each value, so that F_{hol} has been defined as the mean value given by equation (1). With this definition, values of F_{hkl} for $2\pi x$ between 0 and π are the same as for $2\pi x$ between 2π and π, so that only values of $2\pi x$ below 180° need be considered.

At this stage it is convenient to take into account the gradual falling-off in intensity with increase of glancing angle. This is due to many independent factors, such as the effect of electron distribution within the atom. The resultant effect may be expressed in the form

$$I \propto f(\theta),$$

where I is the total intensity of reflexion at a glancing angle θ, and $f(\theta)$ is an unknown function of θ. The intensity of reflexion is also proportional to the number of faces N corresponding to the form $\{hkl\}$. Combining these factors with the phase factor, the intensity of reflexion from a plane (hkl) is given in arbitrary units by

$$I = NF_{hkl} f(\theta). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As a first approximation only, we assume that $f(\theta) = \mathrm{cosec}^2\theta$, as in the case of arsenic (*loc. cit.*). In order to minimise any error introduced by this assumption, only lines in neighbouring portions of the film are compared.

Table II., Column II. gives the values of $\frac{N}{\sin^2\theta}$ for various reflecting planes, and comparing this with Column III. for neighbouring lines, we see that the following conditions must hold :—

1. $(10\bar{1}1)$ is much stronger than $(10\bar{1}0)$; $2\pi x > 64°$.
2. $(1\bar{1}20)$ is far less than half (1011) ;
   $2\pi x$ lies between 42° and 108° or above 132°.
3. $(11\bar{2}0)$ is far greater than twice (2020) ;
   $2\pi x$ lies between 39° and 148°.
4. $(20\bar{2}0)$ is much less than a quarter $(20\bar{2}1)$;
   $2\pi x$ lies between 40° and 140°.
5. $(12\bar{3}1)$ is far less than $(12\bar{3}0)$;
   $2\pi x < 27°$ or $2\pi x$ lies between 55° and 99°.
6. $(11\bar{2}3)$ is not less than (1231) or much more than $(12\bar{3}1)$; $2\pi x$ lies between 22° and 26°, or 77° and 107°.

7. $(12\bar{3}0)$ is very much stronger than $(11\bar{2}3)$;
   $2\pi x$ lies between 46° and 90°.
8. $(30\bar{3}0)$ is less than a quarter $(12\bar{3}0)$;
   $2\pi x$ lies between 25° and 95°, or 149° and 173°.
9. $(30\bar{3}2)$ is greater than $(10\bar{1}4)$;
   $2\pi x < 90°$ or $2\pi x > 152°$.
10. $(13\bar{4}0)$ almost disappears;
    $2\pi x$ lies between 24° and 40°, or 73° and 131°.

Any value of x between 76° and 90° will satisfy all those conditions, so that systems 23 and 24 are possible structures for selenium.

Calculated values for I were obtained by substituting in equations (1) and (2) the values $2\pi x = 80°$ and $f(\theta) = \mathrm{cosec}^2\theta$. Table II., Column V. gives the corresponding order of intensity for comparison with Column III. It is clear that the observed intensities fall off much more rapidly than those calculated from equations (1) and (2); this must mean that $f(\theta)$ has some other value than $\mathrm{cosec}^2\theta$. The theoretical expression deduced by Darwin* for the powder method gives this factor as

$$\frac{1+\cos^2 2\theta}{\sin\theta} e^{-B\sin^2\theta} F,$$

where B is a constant, and F is an unknown function which expresses the effect of electron distribution on the intensity of reflexion. In the present case, it is also necessary to bring in a factor to allow for the greater diffusion of the reflected beam in directions at right angles to the incident beam than in other directions†, so that the expression becomes

$$f(\theta) = \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} e^{-B\sin^2\theta} F. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is impossible as yet to give any value to the factor F in the case of selenium. The only possible method of approach is therefore to find an entirely empirical expression for $f(\theta)$ which agrees with the observed facts and involves no assumptions as to the nature of the function F. Equation (3) suggests several empirical formulæ, of which the following has been found to work best:—

$$f(\theta) = \frac{e^{-B\sin^2\theta}}{\sin^2\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

* C. G. Darwin, Phil. Mag. xliii. p. 800, §§ 4 & 10 (May 1922).

† Compare J. M. Bijvoet and A. Karssen, *K. Akad. Weten. Amsterdam*, xxv. p. 17 (1922).

If we introduce a factor $(1+\cos^2 2\theta)$ into the expression, the intensity does not fall off sufficiently rapidly for $\theta > 45°$. On the other hand, an expression of the form

$$f(\theta) = \frac{e^{-B\sin^2\theta}}{\sin^2\theta\cos\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

fits the data practically as well as that given by equation (4), as is shown below.

Two values of B were substituted in equation (4), and the corresponding values of I were calculated from equations (1), (2), and (4). Giving B either of the values 2·72 and 3·40, the agreement with the observed intensities is good. It is useful, however, to try the effect of varying the value of x within a narrow region in the neighbourhood of $2\pi x = 80°$. If we do so, we find the best agreement for $2\pi x = 78°$ and B = 3·4. For these values of x and B, Column VI. gives the calculated intensities and Column V. the order of intensity. If we take the difference between the observed and calculated orders for each line in turn, the arithmetic sum of these differences is the "Total Error" between the observed and calculated orders of intensity. This value is given in the bottom line of each column. Column VII. gives the actual values of the intensity calculated from equation (4), giving B the value 4·2. It differs very little from Column VI., so that equations (3) and (4) are almost equally applicable. Table III. gives the "Total Error" for varying values of x and two different values of B.

Table III. (Selenium).

Total Error in Order of Intensity for varying values of B and x.

Parameter ($2\pi x$).	70°.	75°.	78°.	80°.	85°.	90°.
B=0	...	...	...	41	...	...
B=2·72.....	20	18	14	14	16	24
B=3·40.....	20	12	10	12	20	24

To sum up, the observed order of intensity of reflexion is consistent with a value of the parameter $2\pi x = 78°$.

B. Tellurium.

5. *Evaluation of the Parameter.*

Tellurium only forms one crystalline modification. It has a density of 6·235 (Kahlbaum) *, 6·338 (Beljankin) †. It is trigonal, being ismorphous with metallic selenium. The commonest forms are {100} and {$\bar{2}$11}. The angle

* Kahlbaum, *Zeitschr. f. anorg. Chem.* xxix. p. 289 (1902).
† *Jour. Phy. Chim. Russ.* xxxiii. p. 670 (1901).

between the rhombohedral axes $\alpha = 86° 47'$, which corresponds with an axial ratio $a : c = 1 : 1{\cdot}3298$ (G. Rose) *. Cleavage occurs most readily along (211), and less readily along (111).

Several photographs were taken, using different specimens of tellurium, with the results tabulated in Table IV.

TABLE IV.

I.	II.	III.	IV.	V.	VI.
			Order of Intensity.		
$\frac{d}{n}$ (Obs.) $\times 10^{-8}$ cm.	$\frac{d}{n}$ (Calc.) $\times 10^{-8}$ cm.	Reflecting Planes.	Observed.	Calculated. B=0.	Calculated. B=2·0.
	5·91	0001	...	...	...
3·845	3·850	$10\bar{1}0$	16	19	14
3·220	3·224	$10\bar{1}1$	1	1	1
	2·957	0002	...	...	...
2·344	2·342	$10\bar{1}2$	2	2	2
2·219	2·222	$11\bar{2}0$	3	5	3
2·078	2·077	$11\bar{2}1$	12	16	13
1·968	1·972	0003	11	13	12
	1·925	$20\bar{2}0$	...	21	20
1·830	1·831	$20\bar{2}1$	5	7	5
1·765	1·778 1·754	$11\bar{2}2$ $10\bar{1}3$	15	15	15
1·614	1·612	$20\bar{2}2$	7	10	7
	1·478	0004	...	...	...
1·464	1·474 1·453	$11\bar{2}3$ $21\bar{3}0$	6	3	4
1·410	1·412	$21\bar{3}1$	9	9	9
1·375	1·380 1·378	$10\bar{1}4$ $20\bar{2}3$	9	11	11
1·308	1·307	$21\bar{2}2$	13	8	10
1·287	1·283	$30\bar{3}0$			
1·255	1·252	$30\bar{3}1$	14	17	16
	1·230	$11\bar{2}4$	...	22	21
	1·182	0005	...	...	...
1·172	1·177 1·172 1·170	$30\bar{3}2$ $20\bar{2}4$ $21\bar{3}3$	4	6	6
1·131	1·130	$10\bar{1}5$	16	14	17
	1·111	$22\bar{4}0$	...	20	22
1·092	1·092	$22\bar{4}1$	18	18	19
1·075	1·075 1·068	$30\bar{3}3$ $31\bar{4}0$	19	12	18
1·051	1·050	$31\bar{4}1$			
1·038	1·042 1·040 1·037	$11\bar{2}5$ $22\bar{4}2$ 2134	8	4	8
		Total Error		42	16

* Pogg. *Ann. d. Phys.* lxxvii. p. 146 (1849).

Column I. gives the observed spacing, the mean values obtained from two films. These fit quite well on Hull's graph for a simple triangular lattice of axial ratio 1·33. The corresponding (hexagonal) indices are given in Column III. Assuming that the atomic weight is 127·5 and the density 6·3, it follows, as in the case of selenium, that there are three atoms associated with each point of the lattice. The calculated spacings after allowing for a slight systematic divergence are given in Column II. The corresponding value of the density is 6·25, and the length of the side of the base of a unit cell $a=4{\cdot}445$ Å. This is in concordance with the results of Miss M. K. Slattery *, who found that the structure of tellurium was based on a triangular lattice of axial ratio $c:a=1{\cdot}33$ and $a=4{\cdot}44$ Å, three atoms being associated with each lattice point.

On comparing Columns I. and II. it is apparent that a a number of lines are entirely missing. This is due to two causes : the films were not so clear as those of selenium, so that the weakest lines did not show up ; but the peculiarities of the structure are also partially responsible. The complete disappearance of (0001) and (0002) offers us the same choice of structure as in the case of selenium. It is interesting that now the (0003) reflexion stands out clearly and is not masked by its coincidence with another line as with selenium. Similar arguments to those used for selenium show that we can reject any other type of structure but Sohncke's point-systems Nos. 19 and 20, and 23 and 24.

The observed orders of intensity are shown in Column IV. and are the mean from three films. In order to test systems 19 and 20 we endeavour to find a value for x, the indeterminate parameter which is reconcilable with the observed intensities. It must fulfil the conditions :—

1. Since $(10\bar{1}0)$ is weak ; $2\pi x=180°$.
2. $(20\bar{2}0)$ invisible ; $2\pi x=90°$.
3. (1011) is very strong ; $2\pi x=180°$.
4. (2021) very strong ; $2\pi x=90°$.
5. (3031) much weaker than $(20\bar{2}1)$ but by no means disappears ; $2\pi x=75°-150°$ fulfils the first condition but (3031) vanishes for all the region around $2\pi x=120°$.

Systems 19 and 20 clearly cannot afford solutions. As

* *Loc. cit.*

with selenium systems 23 and 24 are the only possible arrangements. In confirmation of this we can find a possible value for x which will fulfil the following conditions :—

1. $(10\bar{1}0)$ is weak ; $2\pi x$ lies between 93° and 165°.
2. $(10\bar{1}2)$ is almost equal to $(11\bar{2}0)$; limits are 85°—153°.
3. $(11\bar{2}0)$ greater than $2\times(11\bar{2}1)$; limits are 94°—146°.
4. (0003) greater than (1121) but less than $2\times(11\bar{2}1)$; limits are 97°—104° or 143°—136°.
5. (0003) greater than $(10\bar{1}0)$; limits are 94°—161°.
6. (0003) greater than $3\times(20\bar{2}0)$; limits are 45°—135°.
7. $(20\bar{2}2)$ greater than $(21\bar{3}1)$; $2\pi x$ lies below 96°.
8. (2131) not less than $(10\bar{1}4)$; $2\pi x$ lies below 70° or above 89°.
9. (2240) less than $(22\bar{4}1)$; limits are 17°—43°, 77°—103°, or 137°—163°.
10. (2241) greater than $(30\bar{3}3)$; limits are $2\pi x$ below 98° or above 142°.

A value of $2\pi x$ about 96° or 97° appears quite satisfactory. As before, $f(\theta)$ in equation (2) has been taken to be $\mathrm{cosec}^2\theta$ and to minimize the possible error only neighbouring lines have been compared. All the experimental evidence, therefore, supports the choice of Nos. 23 and 24 for the structure of tellurium as well as selenium. Table IV., Column, V. gives the calculated orders of intensity obtained by the aid of equations (1) and (2), on the assumption that $2\pi x=100°$, and $f(\theta)=\mathrm{cosec}^2\theta$. A better agreement is obtained by the use of equation (4). Column VI. gives the order of intensity for $B=2{\cdot}0$ and $2\pi x=97°$. These values give the best possible agreement with the observed intensities. The "Total Error" is still greater than in the case of selenium, but this is due to the inferiority of the films, in the case of tellurium. Table V. shows the "Total Error" for varying values of B and x.

Table V. (Tellurium).

Total Error in Order of Intensity for varying values of B and x.

Parameter $(2\pi x)$.	90°.	93°.	95°.	97°.	100°.	105°.
B=0	...	...	...	...	42	...
B=1·5	38	26	22	26	26	42
B=2·0	40	34	20	16	34	46

The value of the variable parameter is therefore $2\pi x=97°$.

6. *The Structure of Selenium and Tellurium and its Relation to the Valency of the Elements.*

The results of the X-ray analysis show that the structure of these two elements corresponds with one of Sohncke's point systems, No. 23 or No. 24, whose projection is given in figs. 3 and 5, each figure referring to either system. No distinction has yet been made between the two systems. As far as X-ray analysis can be applied they are identical, and other methods must be employed to decide which is the actual structure. In both cases the atoms are arranged in threefold spirals around the trigonal axes, so that every third atom occupies the same position if projected on to a plane perpendicular to the trigonal axes. Such a structure may be either right-handed or left-handed. The two enantiomorphous systems are Nos. 23 and 24 respectively. It is possible that crystals of selenium and tellurium exist which correspond to each of the two systems. They would of course be indistinguishable by X-rays, but might be recognized by their outward form.

The structure of selenium is peculiar in that each spiral is so isolated from its neighbours. Every atom of selenium touches two atoms in the same spiral and four atoms in adjacent spirals. In the former case, the contact is much closer, the distance from centre to centre of adjacent atoms being 2·32 Å. The distance between atoms in different spirals is 3·49 Å. The difference between these two radii of combination is extremely large, and suggests a much greater cohesion between atoms in the same spiral than between those in different spirals. It is therefore possible that the crystals will tend to grow in the direction of the trigonal axis more readily than in other directions. Such an abnormal development might account for the occurrence of acicular crystals as described by Brown. Again, it is not unreasonable to suppose that owing to the weaker cohesion between neighbouring spirals, these may not always grow side by side to form a single perfect crystal; under certain conditions we may therefore get parallel growths, such as the lamellar crystals of selenium.

It is interesting to regard the structures of selenium and tellurium from a point of view which brings out their relationship to the structures of other non-metallic elements. If the value of the parameter was given by $2\pi x = 120°$, selenium would have the structure of a simple rhombohedral lattice. The unit cell would be a rhombohedron containing one atom, the angle between rhombohedron edges being 92°·42′ in the case of selenium and 86° 47′ in the case

of tellurium. Thus the three interpenetrating lattices of selenium and tellurium fit together to form a structure which is almost simple cubic. In this respect selenium and tellurium resemble the elements of Group V. In the case of Group IV. the structure at first sight appears to be quite different as there is no distortion of the cubic lattice, but the only real difference is in the much greater value of the displacement from the simple cubic lattice. In general, the crystal structure of all elements of Groups IV., V., and VI. hitherto elucidated * is a slightly distorted and internally displaced simple cubic lattice ; the direction of displacement depends only on the valency of the elements.

In a simple cubic structure each atom has six equidistant neighbours. Since none of the atoms at present under consideration can present the same aspect to each of its neighbours, an atom of such a structure will be attracted unequally in different directions. This results in an internal displacement of the structure. The elements of Group VI. have two negative valencies, and each atom is in consequence drawn towards two of its neighbours. An atom of selenium or tellurium may therefore be displaced along any digonal axis of the simple cubic lattice. Actually the atoms of one crystal are only displaced in one of three directions, each perpendicular to the same trigonal axis, and making angles of 120° with the other two. Atoms constituting a triangular lattice with its trigonal axes perpendicular to the direction of displacement are shifted in the same direction. In the case of selenium the whole structure suffers a contraction, and in the case of tellurium an elongation, parallel to these trigonal axes. The trivalent atoms of Group V. are displaced towards three neighbours by movements along a trigonal axis, half the atoms, constituting a face centred lattice, being moved in each direction. The whole structure is again elongated parallel to this axis.

In the case of the tetravalent elements of Group IV. the displacement follows the same course. It is clearly impossible for an atom of a simple cubic structure to be shifted towards more than three of its six neighbours simultaneously. The displacement therefore proceeds as for a trivalent element, but continues beyond the point when each atom is co-planar with the three nearest atoms, so that it now approaches a fourth atom. Finally, each atom has four equidistant neighbours. Graphite does not conform to this type ; each atom has three equidistant neighbours.

* Lead and white tin are exceptions.

Debye * and Hull † give two different arrangements, and which is the correct structure is still uncertain.

With this exception, in the normal crystalline forms of carbon, silicon, germanium, grey tin, arsenic, antimony, bismuth, selenium, and tellurium, electron sharing takes place until the outer shell of each atom has its full quota of electrons. In this way each atom of these elements is in close contact with as many neighbours as it has negative valencies. These elements are on the whole non-metallic in their chemical and physical properties. The exceptional structure of lead and white tin is consistent with their predominantly metallic characteristics. The accompanying plate (Pl. X.) shows models of the structures of arsenic and selenium. The atoms are represented by spheres in contact with each other. In order to represent close contact the spheres are cut away at the points of closest approach.

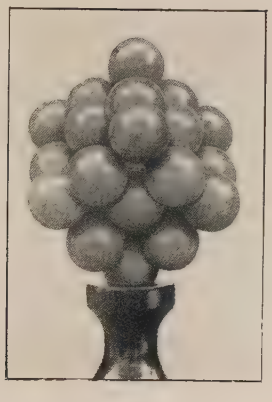
Summary.

The structures of metallic selenium and of tellurium were determined by the powder method of X-ray crystal analysis; they may be regarded as simple rhombohedral structures with interaxial angles of almost 90°, in which each atom is slightly displaced towards two of the six adjacent atoms. The resulting structure is a threefold spiral, composed of three interpenetrating simple triangular lattices. It therefore allows of two enantiomorphous forms, which are indistinguishable by the methods of X-ray analysis.

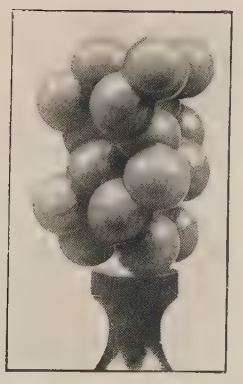
The crystal structures of elements of Groups IV., V., and VI. differ from group to group in virtue of the difference in negative valency, which regulates the direction of displacement from the simple cubic structure which is the basis of the atomic arrangement. Elements in the same group differ in the extent of displacement, the heaviest atoms being the least shifted.

The author thanks Professor Bragg for his kind advice throughout the progress of this research, and again acknowledges his indebtedness to Dr. Brentano for his invaluable help and advice, especially in the initial stages of the work. Part of the apparatus used was purchased from money kindly given to the Physical Laboratory by the Government Grant Committee of the Royal Society, and by Messrs. Brunner Mond. The author is in receipt of a grant from the Board of Scientific and Industrial Research.

* Debye, *Phys. Zeit.* xiii. p. 297 (1917).
† Hull, Phys. Rev. x. p. 662 (1917).



Arsenic.



Selenium.

LI. *An Experimental Study of Grating Errors and "Ghosts."* *By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University* *.

[Plate XI.]

THE work to be described in the present paper was undertaken in the course of a study of the problem of making short-focus concave gratings for vacuum spectrographs. Since assuming charge of the Rowland dividing engines in the spring of 1923, I have investigated a number of the more or less obscure matters relating to diffraction gratings. The cause of the Lyman ghosts has been ascertained experimentally, and an attachment added to the engine which has abolished them completely. An optical method of studying the errors, periodic and otherwise, of gratings has been developed, which can be applied to any grating, either plane or concave. This method, while lacking some of the advantages of the method of cross-ruling, first suggested by Lord Rayleigh and employed by Rowland, is more sensitive than this, and will show the effect of two or three slightly misplaced lines, on a grating ruled with 15,000 lines to the inch. It has made possible the examination of the effects of stopping the machine for a few minutes during the process of ruling, throwing the thermostat out of action, opening the case and oiling the machine, etc. The method has, in addition, furnished experimental data which make it possible to visualize, so to speak, the manner in which the "ghosts" or spurious lines are produced, when a periodic error of ruling is present in the grating. The method consists of a photographic (or visual) determination of the intensity variations across the diffracted wave-front when the grating is illuminated with monochromatic light from a slit. If we examine the wave-front with a short-focus lens used as an eyepiece, at a distance of say 20 to 40 cm. from the grating we shall find the luminous field crossed by a multitude of vertical black lines arranged more or less in periodic groups. A brilliant source of light must be employed behind the slit. A quartz-mercury arc is best, and no lenses are employed. If a photographic plate is substituted for the eyepiece, we obtain a permanent record of the bands which can be studied at leisure. These bands can be observed on the wave-front almost up to the surface of the grating, becoming finer and more numerous as we approach the ruled surface.

* Communicated by the Author.

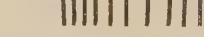
If a concave grating of short focus (say 1 metre radius of curvature) is examined in this manner, it will be found that, at a distance about half-way from the grating to the focus, the light has gathered itself into very bright vertical bars, the spaces between being quite black, the distance between the bars corresponding to the pitch of the screw of the dividing engine, reduced of course by the converging action of the grating. On moving the eyepiece back towards the focus these bars disappear gradually, the wave-front becoming nearly uniform in brilliancy. Still farther back the bars appear again, only to vanish once more as we near the focus. These same bars are seen with a plane grating used in conjunction with lenses in the usual manner.

On Pl. XI. figs. 1 to 7 reproductions are given of the photographic records obtained with a small concave grating of 1 metre radius, ruled with 15,000 lines to the inch. The slit was backed by a quartz-mercury arc, and the plates exposed at the recorded distances from the grating. A cell containing a dilute solution of copper chloride, placed close to the slit, cut off all radiations of shorter wave-length than 4358; the green and yellow lines are inoperative if ordinary plates are employed.

These photographs will doubtless come as a surprise to the reader who is accustomed to think of the diffracted wave-front as differing in no respect from ordinary wave-fronts of uniform amplitude—a condition that would obtain only in the case of a perfect grating, free from periodic errors of ruling.

The grating used in making these photographs had a periodic error somewhat in excess of those usually ruled. The reproductions have been enlarged three-fold from the original negatives, which were obtained by simply mounting a photographic plate in the path of the converging diffracted wave-front, at different distances from the grating. At 28 cm. and 60 cm. the bands are most distinct, the region between the luminous bars being almost black. At 55 cm. and 64 cm. they have practically disappeared, the illumination across the wave-front being nearly uniform.

These bright bars of light we may consider as formed in the following way. A single periodic error, such as results from a slight eccentricity of the large wheel with its 750 teeth, which turns the screw, gives us a grating in which the lines, instead of being equidistant, are arranged thus



this pattern repeating itself across the grating at intervals equal to the pitch of the screw. Now it is well known that

a grating in which the lines are ruled closer and closer together as we pass across its face has focal properties—that is, it exercises a converging or diverging action on the diffracted rays, according to whether we observe on the right or left of the central image. This action was first noticed by Cornu, and is fully treated in my 'Physical Optics,' the grating acting in a manner analogous to a zone-plate. Now in the present case we have this type of spacing, but reversed in direction at regular intervals; consequently the grating is made up of alternate linear elements, of which one set converges slightly, while the other diverges, the diffracted rays from the directions which they would have if the grating were perfect. The effect is more marked if the diffracted wave-front is already converging, as is the case with a concave grating. We can show the first system of bright bars by drawing a ray diagram for a grating of this type and its disappearance further on. Its subsequent reappearance involves an interference phenomenon, and cannot be shown very well by rays.

We will now take up the relation between these bars of light and the "ghosts" which accompany the spectrum lines when a periodic error is present in the grating. The very elementary explanation of the production of ghosts which I gave in 'Physical Optics,' is based on a type of periodic error which never occurs in practice, namely an extra line introduced at regular intervals. This can be accomplished experimentally by superposing a fine and a coarse grating. The spectrum lines given by the fine grating are accompanied by lateral spectra due to the coarse grating, forming the "ghosts." If we regard the coarse grating in the light of a periodic error, it is easy to visualize how the ghosts are produced. In practice, however, the error is a gradual change in the distance between the lines, and the analytical treatments are not very helpful in enabling us to form a picture of what is actually taking place. Our experiment shows us, however, that the wave-front at certain distances from the grating is broken up into vertical bars of light, separated by dark intervals of about the same width as that of the bright bars—in other words, not very different from an ordinary wave-front, *after it has passed through a number of parallel slits, in an opaque screen.* Following such a wave-front to the focus, we find a central image and lateral spectra. The "ghosts" correspond to these lateral spectra. We thus see that the periodic error has impressed upon the wave-front a condition similar to that produced by its passage through a coarse grating acting by opacity.

To test out this theory of the formation of the "ghosts," I tried intercepting the wave by a slit which could be made of such width as to transmit one, two, three, or more of the bright bars on the wave-front. We know, from the theory of the grating, that there are secondary maxima between the principal maxima to the number of $n-2$, n being the number of lines in the grating. This was found to hold also in the present instance. If the slit transmitted four of the bright bars only, there were two faint maxima between the main line and each ghost to its right and left. It was found also that, at the second reappearance of the bright bars as we move back towards the focus, the number was always one less than the number transmitted by the wide slit. A somewhat similar effect is observed also when a converging wave-front of monochromatic light is passed through three or four narrow parallel slits, the phenomenon being related to the well-known periodic appearance and disappearance of the structure of a wire grating when viewed by transmission with monochromatic light at increasing distances. This treatment of the formation of ghosts enables us to see also why the ghosts of the first and third order are strong, while the second-order ones are very faint or absent. This is, at least, the case with all gratings ruled on the Rowland engines. From grating theory we know that if the widths of the transparent and opaque parts of a grating are equal, the spectra of even order are not present, since they lie in the directions of the diffraction minima of one of the transparent slits when operating alone. The vertical dark and light bars on the wave-front are of very nearly the same width; hence the ghosts of even order vanish. This point was verified by mounting a needle-point in coincidence with the point at which the second-order ghost would appear if present. The diffracted wave-front was now screened off with the exception of a single bright bar, and the needle-point was found to be exactly at the centre of one of the first lateral minima bordering the central maximum of the fringe system of Fraunhofer's first class, formed by a single slit.

As it sometimes happens that the ruling is interrupted by failure of the electric power, the method was used for a study of the effect of this accident on the ruling. The room in which the engine is operated is kept at a temperature constant to within 1° C. month after month, by a small gas-stove controlled by a toluene and mercury thermostat. The temperature within the glass case, in which the engine operates, is now kept constant to within 0°·1 C. by electric heating, controlled also by a thermostat. The air in the room is kept

in constant circulation by an electric fan, and the products of combustion from the gas-stove are carried out of the room by a long stove-pipe, which distributes the heat of the stove over a wide area. A test ruling was made on a flat plate, and after the machine had been in operation for three hours, the motor was stopped for fifteen minutes, and then started again.

Fig. 13 (Pl. XI.) is a photographic record (enlarged three times) of the wave-front at a distance of 60 cm. from the grating, the black and white bar at the centre resulting from a local change in the ruling, due to the stopping of the machine. On examining the wave-front (green mercury light) with an eyepiece, it was found that this singularity could be followed right up to the grating, *i.e.* with the eyepiece practically focussed on the ruled surface. It appeared as a very fine vertical black thread running right across the ruling parallel to the lines. One would almost take oath that at least fifteen or twenty lines were missing altogether. On moving the eyepiece back, the line broadened and a faint black "satellite" split off from it, moving slowly across the grating in the direction in which the ruling had continued after the stopping of the machine.

It appeared important to determine, if possible, just what had happened to the grating at this point. I found that the black line could be seen if the grating was examined with a short-focus lens in the light of the third-order spectrum of a lighted window. Its position was indicated on the grating by a minute ink dot, which was then brought into the field of a microscope, illuminated with vertical light (green mercury line) from a transparent reflector just above the objective. To my surprise, instead of finding a narrow strip devoid of ruling as I expected, I found nothing peculiar in the ruling except that there were two lines somewhat closer together than the others.

By placing a horizontal slit in front of the reflector, I succeeded in so controlling the illumination that the ruling appeared as very narrow green lines separated by wide black intervals. A photograph obtained with a $\frac{1}{2}$-inch oil-immersion objective is reproduced on Pl. XI. fig. 12. The lines were ruled from right to left, the point at which the machine was stopped being indicated by an arrow. The next line ruled is a little closer to its right-hand neighbour than it should be, after which the grating space is slightly greater than the normal for several lines, to make up for the narrow interval, the lines coming into their correct position again presently. This was shown by measuring the photograph

on a dividing engine. To explain this we must suppose that on stopping the engine the carriage moves back a little, so that the next advance by the turn of the screw does not bring it to its correct position. A possible explanation may be that during the fifteen minutes of repose, the oil film between the screw and the nut was squeezed out, and since the nut is pushed forward by the front surface of the threads, this would cause the nut to retreat slightly when the oil film was removed. On starting the machine, oil is carried gradually into the spaces again, driving the nut and carriage forward, and giving a slightly increased spacing over that caused by the turning of the screw. This explanation is the only one that I can think of, and it may be found quite out of accord with what is already known about lubrication.

When we remember that the grating is ruled with 15,000 lines to the inch, it seems remarkable that the slight displacement of half-a-dozen lines causes a local change of illumination that can be seen on the face of the grating, with a lens of 1 inch focus used as a hand magnifier. As a matter of fact, we probably see the black line not really on the surface of the grating, but at a little distance in front of it, where the effect has spread by diffraction.

I was interested in seeing whether this local error affected the resolving power of a small strip of the grating embracing it. A slit 1 mm. in width limited the wave coming from the collimator of a spectroscope. This, however, covered enough lines on the grating to resolve the yellow mercury lines; no change in the resolution could be detected between the region containing the local errors and the rest of the surface. This shows us, in a different way, that only a very few lines are out of place, and we may infer from this that stopping the machine, for a short time at least, ought not to impair the resolving power. Cross rulings, however, show that we ought not to begin ruling until after the machine has been running for two or three hours.

I have examined, by the wave-front method, three very fine plane gratings ruled by Dr. Anderson on the same machine some ten years ago. These gratings are probably the best that have ever been ruled; one has five inches of ruled surface (75,000 lines), the other two seven inches, or 105,000 lines. They all have very nearly, if not quite, their full theoretical resolving power, and the ghosts are very faint, due to Dr. Anderson's skill in so adjusting the machine that the periodic error of the screw was practically compensated by introducing a slight eccentricity of the toothed wheel. A photograph of the wave-front from

the five-inch grating is reproduced on Pl. XI. figs. 10–11, the upper figure natural size, the lower enlarged a little over three-fold. Here we see a systematic interruption of the regularity of ruling which occurs about every twelve turns of the screw. The lower figure shows the region between two of these dark bars, and indicates how the wave-front is torn to pieces by errors of spacing, even in the case of a very perfect grating. Comparison of figs. 11 and 13 would lead one to infer that the machine had been stopped twice each day during the ruling, but this is hardly likely. It will be noticed that the dark bars are not exactly equidistant, as they would be if they were due to two periodic errors getting in step at regular intervals.

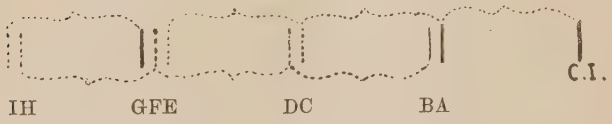
We will now take up the question of the "Lyman ghosts."

The Lyman Ghost.

As is well known, periodic errors of ruling produce spurious lines or "ghosts" of two types, the so-called Rowland ghosts, first described by Quincke, which are symmetrically spaced to the right and left of, and close to, the strong lines of the spectrum, and another type, first observed and studied by Professor Lyman of Harvard University. These latter are more troublesome, as they are distributed at wide intervals, filling up the region between the central image and the first-order spectrum, and hence mingling with the lines of the spectrum investigated with vacuum spectrographs. Three papers appeared in the 'Journal of the Optical Society of America' for 1922 dealing with these ghosts, an experimental study by Meggers and Kiess, an analytical treatment by Runge, and a discussion of the sources of periodic errors of ruling engines by Anderson. As it appeared from these papers that two periodicities, in addition to the normal periodic error (which has a period equal to the pitch of the screw), were required for their production, and as one of these periodicities showed variation from time to time on the same machine, it was first necessary to determine their value at the present time. The slit of the vacuum spectrograph was illuminated by monochromatic light obtained from a cadmium spark by a quartz spectroscope. The instrument was not exhausted, and the concave grating of one metre radius was so adjusted that the central image fell just within the edge of the plate. Exposures of half an hour were given, ordinary plates being employed.

The Lyman ghosts appeared as in fig. 1.

Fig. 1.



On measuring the distances of these lines (which are all formed by light of a single wave-length) from the central image, it was found that the distances from C.I to A, from A to C, and from C to E (E very faint) were equal. A, C, and E can thus be considered as first-, second-, and third-order spectra produced by the smaller periodicity. This was found to correspond to five lines of the grating, as in the cases considered in the papers referred to. The distance between A and B and between other adjacent lines of the groups gave a periodicity equal to 88 lines of the grating.

If we compare these ghosts with the Rowland ghosts as ordinarily found, we observe this difference. The latter are very faint and are symmetrical about the strong spectral lines of different orders. If, now, we try to picture the formation of the Lyman ghosts in the same way, we might expect the periodicity of five grating lines to produce strong spectral lines of order 1, 2, 3, etc., accompanied by fainter companions (analogous to the Rowland ghosts) due to the 88-line periodicity. This is not the case, however, as is seen from fig. 1, in which constant distances between lines are indicated by brackets. We should have a very similar condition if, in a system of spectra of various orders (of monochromatic light), we considered that the Rowland ghosts to the right of the main lines gradually died out as we ascended to higher orders, while those to the left increased in intensity until they surpassed the intensity of the main lines, which also die out in their turn. Rowland showed that similar effects were obtained with gratings ruled on the machine before the errors had been ground out of the screw, the ghosts often being stronger than the main lines.

Having determined the two periodicities responsible for the ghosts, a search for their source was made. Anderson had suggested that the five-line periodicity was accounted for by the circumstance that the driving-belt made two revolutions for every 5+ cycles of the machine, a distortion of the

whole machine resulting from the passage of thicker portions of the belt over the pulleys.

To study this matter in detail, a white mark was made on the large driving-pulley of the machine and another white mark on the belt, the two marks being in coincidence. The engine was then started. After one revolution of the belt, the pulley had made 2·5 revolutions, and the mark on the belt met the pulley on the side opposite to the white mark. After another revolution of the belt, the two marks came nearly, but *not quite* into coincidence. With each further double revolution of the belt, the marks drifted further apart, coming into coincidence again after 87 revolutions of the pulley. Since one line is ruled for every revolution of this pulley, we see at once that both periodicities are accounted for: the five-line one corresponds to the circumstance that a given point (say a thicker portion) of the belt is somewhere on a specified semicircumference of the pulley once in every 5+ revolutions; the 87-line one to the circumstance that the given point of the belt engages the same spot on the pulley once in every 87 revolutions. It follows from this that a coincidence of a thick spot on the belt with the very small motor pulley at the moment when the screw is advancing the carriage, will also occur once in every 87 cycles of the machine. The five-line periodicity suggests a slight eccentricity of the large driving-pulley.

In a paper on the vacuum spectrograph (Phil. Mag., Nov. 1923) I stated that the Lyman ghosts appeared to be developed with greater intensity with ultra-violet light of very short wave-length, since they were obtained with a five-minute exposure with the spark, while the mercury arc, screened with a filter of nickel glass (transparent to 3663), gave no trace of them, even with an exposure of half an hour. Their failure to appear in the latter case, I have since found was due to the fact that with the arc the wide cone of light entering the slit was in part diffused back to the plate by the inner wall of the spectrograph, fogging the plate, and prevented the faint ghosts from registering. By diaphragming the quartz-mercury arc so that the cone barely filled the grating, a profusion of ghosts appeared. The region between wave-lengths 700 and 1500 Ångströms is reproduced on Pl. XI. fig. 14 *b*. In coincidence with this spectrogram is another (*c*) made with the filter of nickel glass, which transmits only the mercury triplet 3650–3654–3663.

These are four-fold enlargements of the original negatives. The central image lies to the left, at a distance about equal

to the length of the spectrum reproduced. The approximate wave-lengths of real lines of the first-order spectrum, occupying the positions of the mercury triplet ghosts, are 730 Å.U. and 1460 Å.U. Time of exposure to quartz Hg arc, ½ hour. It was found that if a longer driving-belt was used, the slack being taken up by an idle pulley, the ghosts appeared in totally different positions, the spectrum of the ghosts of the total radiation of the mercury arc bearing no resemblance to the one reproduced, as was to be expected.

The method of driving the machine was now modified in the following way:—A pulley of the same size as the driving-pulley of the engine was mounted close to the latter on a separate support, the two being attached or "coupled" by means of six very thin rubber bands, attached to projecting studs on the two pulleys. This is essentially the same method which I devised for driving a 20-inch mercury reflecting telescope (Astrophys. Journ., March 1909).

A grating ruled under these conditions was exposed for two hours in the spectrograph, the photograph showing only a very faint continuous band with no trace of the ghosts. Another grating, ruled under similar conditions, which showed traces of diffused light between the central image and the first-order spectrum when examined with the eye in sunlight, gave, with an exposure of one half hour in the spectrograph to the quartz Hg arc, a band made up of some 1500 very fine faint lines, so close together that it is very doubtful if any trace of them will appear in the reproduction (Pl. XI. fig. 14 *a*). This grating is of the type usually described as "scratchy," from the circumstance that the diffused light comes from narrow linear areas distributed in a quite irregular manner. I have not as yet determined positively the cause of this phenomenon, which is usually attributed to a breaking-down of the ruling edge of the diamond.

Photographs were made of the wave-fronts from two 1-metre concave gratings—one ruled with the elastic drive, and the other before the attachment had been applied. These are reproduced on Pl. XI. figs. 8 and 9, the former made with the grating free from Lyman ghosts. The latter shows apparently the combined effect of the engine periodicity and the ones introduced by the belt.

Metallized Glass Concave Gratings.

The continuous use of a concave grating in a vacuum spectrograph has been found by Millikan and others to result in a deterioration of the surface caused by products of the electric discharge.

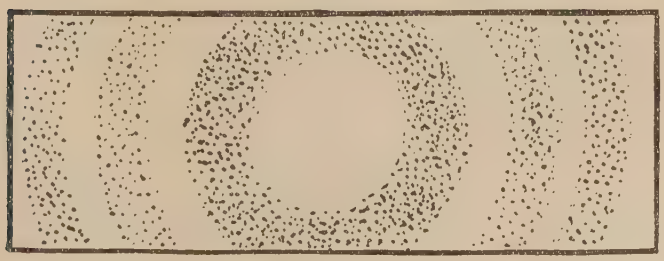
Millikan has stated that it was necessary to rule a new grating every few days for work in the region of the extremely short waves.

To overcome this difficulty, I propose to rule concave gratings on glass, etch them by the method which I described in the Phil. Mag. for Dec. 1906, and then deposit a metallic film on them. The difficulty in ruling glass gratings is due to the breaking-down of the diamond edge. If the pressure is *very* light, this does not happen, but no trace of the grating can be seen, or at most a spectrum so faint as to be almost invisible. Etching with very dilute hydrofluoric acid for a minute or less gives us a grating yielding spectra of great brilliancy. I have already etched a $\frac{1}{2}$-metre concave grating ruled on glass which looks very promising. This grating, when coated with a suitable metallic film by cathode discharge, should prove equal or superior to the ones ruled on speculum metal. When tarnished, they can be cleaned with acid, and given a fresh film of metal. Experiments along these lines will be taken up in the autumn.

Target Pattern.

Short-focus concave gratings, when examined by reflected light, especially in the higher orders of spectra, exhibit a circular target pattern similar to fig. 2.

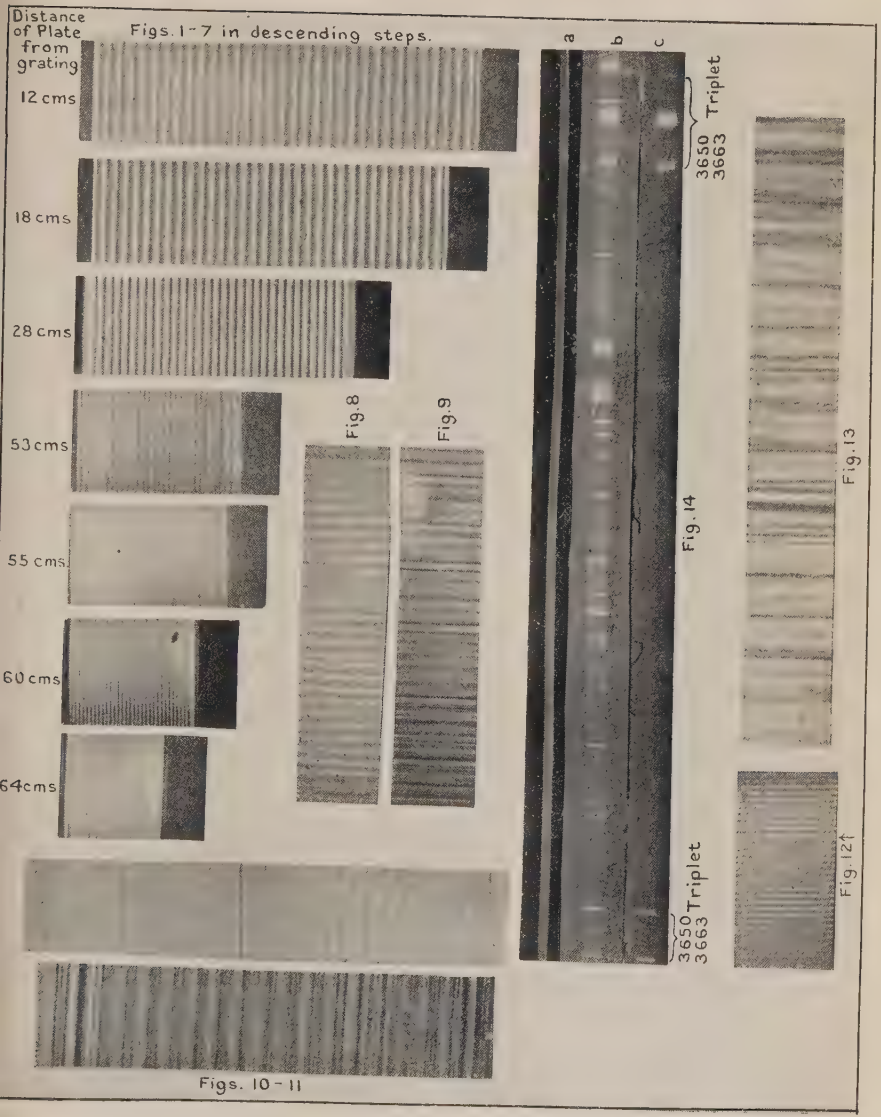
Fig. 2.



If monochromatic light is employed the rings are alternately bright and dark, while white light gives coloured rings, the even rings being red, the odds ones green, for example.

These rings are interesting as showing how the intensity distribution among the various orders varies with the part of the diamond edge used for the ruling. The ruling is done with one of the natural *curved* edges peculiar to the diamond, the edge being set parallel to the direction of the ruling. The diamond is mounted at the end of a horizontal lever ; consequently the *point* on the curved edge which comes in contact with the speculum plate varies with the distance through which the diamond drops before meeting the surface. With a plane grating, sloping uphill slightly in the direction in which the diamond moves when ruling a line, the diamond will be raised by degrees as it draws its line, and the point of contact will travel a trifle along the edge. A grating ruled under such conditions will have, say, the third order bright along one edge, and the fourth order bright along the other, due to the fact that different points on the curved edge of the diamond rule grooves of different form. In the case of a concave grating the diamond falls and rises as each line is drawn ; consequently the form of the groove varies along each line in the same manner. The locus of areas on the grating at which the ruling has been done with the same point on the curved edge of the diamond, is obviously a system of concentric circles. If the grating is not mounted level in the machine, with the centre of curvature at the middle point of the ruling, we have arches of colour instead of circles on the grating.

The concave gratings ruled on Lord Blythwood's machine at the National Physical Laboratory, at least the few which I have seen, show these patterns in a very irregular form, portions of hyperbolæ etc. which I cannot explain. Their cause is doubtless obvious to anyone familiar with the mechanism by which the diamond is lowered in this engine. The existence of this target pattern must be considered in connexion with the resolving power, since certain areas of the grating are inoperative, at least when working with higher orders than the first. The pattern figured is for a grating of 1 metre radius with $3\frac{1}{2}$ inches of ruled surface, viewed in the fourth-order spectrum. In the first order the central circle covers about three-quarters of the grating.


Distance of Plate from grating
Figs. 1-7 in descending steps.
12 cms
18 cms
28 cms
53 cms
55 cms
60 cms
64 cms
Fig. 8
Fig. 9
a
b
c
3650
3663
Triplet
Fig. 14
3650
3663
Triplet
Fig. 13
Fig. 12
Figs. 10-11

LII. *On the Origin and Nature of the Long-range Particles observed with sources of Radium C. By* Sir E. Rutherford, *F.R.S., Cavendish Professor of Experimental Physics, and* J. Chadwick, *Ph.D., Fellow of Gonville and Caius College, Cambridge* *.

§ 1. During the last few years much attention has been directed to an examination of the long-range particles which appear when a strong source of α-rays bombards different materials. In this way, definite proof has been obtained that the nuclei of a number of elements are disintegrated by the bombardment of α-particles with the emission of swift hydrogen nuclei.

In the early experiments which led to the discovery of the artificial disintegration of nitrogen, Rutherford † observed by the scintillation method that the passage of α-particles from radium C through nitrogen and oxygen gave rise to some swift particles which had an equivalent range in air of about 9 cm., compared with that of 7 cm. for the colliding α-particles. Just beyond the range of the α-particles from radium C, the scintillations due to these particles are in general brighter than those due to H nuclei and more resemble those of α-particles.

It may prove of some interest to give a brief account of the somewhat chequered history of subsequent attempts to fix the nature and origin of these long-range particles of 9 cm. range. It was natural at first to suppose that these scintillations were due to a new group of α-particles arising from the source itself; but by examining the alteration of the range of the particles by the addition of thin sheets of aluminium and gold close to the source, it was concluded—erroneously as we shall see later—that the particles did not arise from the source but from the volume of the gas. If this were the case, the scintillations might be due to atoms of nitrogen and oxygen set in rapid motion by close collisions with the α-particles, for the number and range of the particles were of about the magnitude to be anticipated on this point of view. To settle this point, experiments were made to measure the deflexion of the particles in a magnetic field. The mass of the particles could only be estimated by comparing their deflexion in a

* Communicated by the Authors.

† Phil. Mag. xxxvii. p. 537 (1919).

magnetic field with that of other known particles which were similarly produced throughout the volume of the gas. For this purpose, the deflexion in a magnetic field of the particles of 9 cm. range was compared with that of H nuclei set in motion by the passage of α-particles through a gas containing hydrogen. The experiments were difficult, as the number of particles under the experimental conditions was too small to give a sharply marked pencil of rays, but it was found that the particles, although less deflected than the H nuclei, were more deflected than was to be anticipated if they consisted of nitrogen or oxygen atoms carrying a single charge. It was estimated that the particles were probably atoms of mass about 3 carrying a double charge.

Some time later, measurements were made to determine the mass of the particles of range 11·5 cm. emitted by thorium C, which are given out in relatively greater numbers than the 9·3 cm. particles from radium C *. Their deflexion in a magnetic field indicated that they were α-rays of mass 4 This result raised the serious doubt whether the 9·3 cm. particles were not after all α-rays of mass 4. This doubt was increased on finding that the relative number of these particles was independent of the nature of the gas surrounding the source of radium C; for example, within the experimental error the number was found to be the same in air, nitrogen, oxygen, carbon dioxide, sulphur dioxide, and chlorine, and the ranges in these gases were equivalent to that in air when due allowance was made for the stopping powers of the various gases.

Experiments were then made to find if definite proof could be obtained whether the particles were emitted by the source or whether they arose in the gas surrounding it. For this purpose the ranges of the particles were measured in air after passing through absorbing sheets of aluminium, silver, and gold of known stopping powers. It was found, however, that the imperfections of these foils due to holes, even when a large number of thin sheets were placed one behind the other, were too great to permit any definite conclusions to be drawn, and the experiments were abandoned.

Finally, however, by the use of a shadow method—described later in this paper—definite proof was obtained that the particles observed in oxygen had their origin in the source and not in the gas. The conclusions reached at this stage were briefly mentioned in an address † before the Chemical

* Rutherford, Phil. Mag. xli. p. 570 (1921).

† Rutherford, Journ. Chem. Soc. 121. p. 413 (1922); 'Nature,' 109. p. 616 (1922).

Society, republished in 'Nature,' and are shown in the following quotation :—

"The next question which arises is whether any other particles besides that of hydrogen can be released by α-ray bombardment. Some time ago, I found that when radium C was used as a source a small number of bright scintillations was observed, which had a maximum range in air of about 9 cm. It was natural at first to suppose that these were due to a new type of α-rays from the radioactive source. The effect, however, of aluminium screens in reducing the range of these particles led me at first to believe that they were generated in the volume of the gases used, namely, nitrogen and oxygen. By comparing the bending of these rays in a magnetic field with those of H particles from hydrogen, I concluded that they must be atoms of mass about 3 carrying two positive charges. Later experiments have brought home to me the untrustworthiness of this method of fixing the source of the radiation on account of the marked variation in thickness of films of metal foil. Using a more direct and simpler method, I have recently convinced myself that, at any rate in the case of oxygen, the particles have their origin in the radioactive source and not in the volume of the surrounding gas. Under such conditions, the comparative method of estimating the mass of the particles is no longer trustworthy. While a large amount of experiment will be required to fix definitely the nature of the radiation, the general evidence indicates that it consists of particles of mass 4, which are projected from the source and represent a new mode of transformation of radium C."

At the time, attention was directed to experiments on the artificial disintegration of elements by α-rays, and further investigation of the nature of the long-range particles was postponed to a more convenient season.

During the past year Bates and Rogers *, in this laboratory, have made a detailed search for the presence of long-range particles from radium C, thorium C, actinium C, and polonium. In addition to the particles of 9·3 cm. range under discussion, they found evidence in radium C of other groups of particles of the α-ray type, smaller in number and of ranges 11·2 and 13·3 cm. Similarly, groups of particles were observed from the other sources examined.

In view of the fact that the numbers of particles in these groups are of the same order as those to be expected if artificial disintegration were produced in the matter in the

* Bates and Rogers, Proc. Roy. Soc. A, 105. p. 97 (1924).

path of the α-rays, it has become a problem of immediate importance to settle definitely the origin and nature of these particles. We give in the present paper an account of a number of experiments which deal with this question. Our attention has been confined to the groups of long-range particles from radium C, since the active sources used in experiments on artificial disintegration usually consist of this material. We have examined carefully the number and range of the particles that appear when the α-rays of radium C pass through different materials, viz., helium, oxygen, carbon dioxide, xenon, silica, and mica. We have examined also whether the observations are influenced by the mode of preparation of the source, and whether the particles appear in a vacuum. We have also devised experiments to fix the origin of the particles, and to determine accurately the mass and velocity of the particles by measuring their deflexion in a magnetic field.

As a result of these experiments, we have obtained convincing evidence that the long-range particles from radium C of 9·3 and 11·2 cm. range are α-particles of mass 4 which have their origin in the source itself, and not in the surrounding matter. These particles, which appear whatever the material used to absorb the main beam of α-rays, are to be regarded as two groups of swift α-rays which are ejected from the product radium C, and probably represent new types of disintegration of that element.

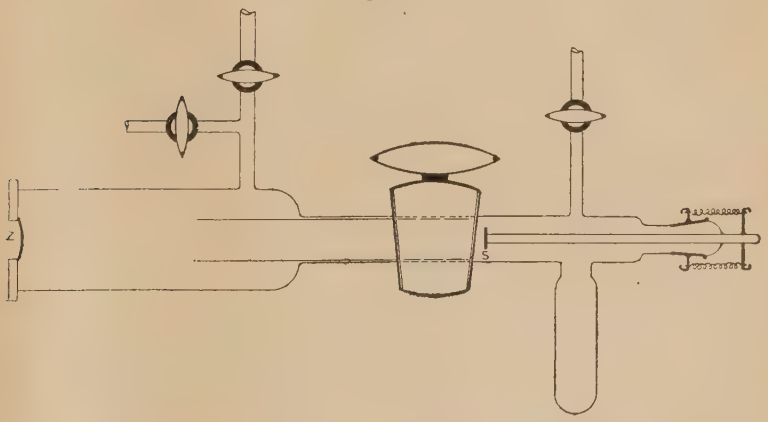
§ 2. *Examination of the Particles in different Gases.*

The earlier observations of one of us have shown that the particles of range 9·3 cm. are present when the α-rays of radium C pass through nitrogen, oxygen, carbon dioxide, sulphur dioxide, chlorine, and boron trifluoride. We have extended these observations by comparing the number of particles obtained when the α-rays were absorbed in helium with those obtained in oxygen, and examined the variation of the number of particles with increasing absorption in xenon, carbon dioxide, and some solids.

The comparison of the particles obtained in helium and in oxygen was carried out with the apparatus shown in fig. 1. It consisted of a long glass tube divided into two compartments by means of a tap of wide bore. The zinc-sulphide screen Z was fixed to the glass plate closing the end of the tube. It was protected from light emitted by the source or any material bombarded by the α-rays by a very thin foil of aluminium. The source, S, of radium B + C was introduced

on the other side of the tap by means of a ground-glass joint. The parts of the tube close to the source were lined with brass in order to avoid the production of H particles from the materials of the glass. The distance between the source and screen was 35 cm. The apparatus was placed between the poles of a magnet to deflect the β-rays from the screen. After placing the source in position and evacuating the apparatus, purified helium was admitted to such a pressure (about 80 cm. of mercury) that the α-particles of 7 cm. range in air were completely absorbed. It was found that scintillations still appeared on the screen to the number of 1·2 per minute per mg. activity of the source. When the

Fig. 1.



pressure of helium was increased to correspond to a range in air of 9·5 cm. most of these scintillations disappeared, the remainder amounting to about 0·2 per minute per mg.

By turning the tap in front of the source, the natural effect of the screen could be counted at any time during the experiment, and the presence of contamination immediately detected. This radioactive contamination, due sometimes to traces of emanation but more often to volatilization or removal of active deposit, is a source of great trouble in experiments of this kind, where the particles to be observed are an exceedingly small fraction of the number in the main group of α-particles. It is our general experience that when contamination occurs the experiments must be abandoned.

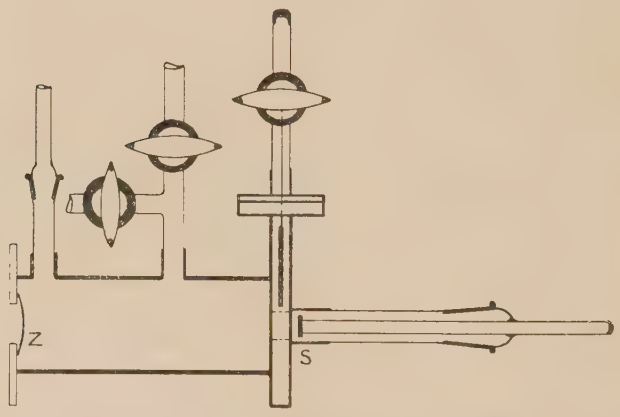
The helium was then pumped out and dry oxygen introduced to the appropriate pressure, and the long-range particles were again counted. The number observed was 1·0 per minute

per mg., decreasing to about 0·2 per minute per mg. when the pressure was raised to correspond to a range in air of 9·5 cm.

Within the accuracy of experiment, then, the number of long-range particles is the same in helium as in oxygen. The area of the screen observed in these experiments was approximately 40 sq. mm. and its efficiency about 70 per cent. The total number of long-range particles emitted by 1 mg. of radium C is therefore about 1100 per second. About one fifth to one sixth of these have ranges greater than 9·5 cm. of air.

Owing to the great stopping power of xenon for α-particles, the experiments with this gas could be performed with a small distance between the source and screen, and the examination

Fig. 2.



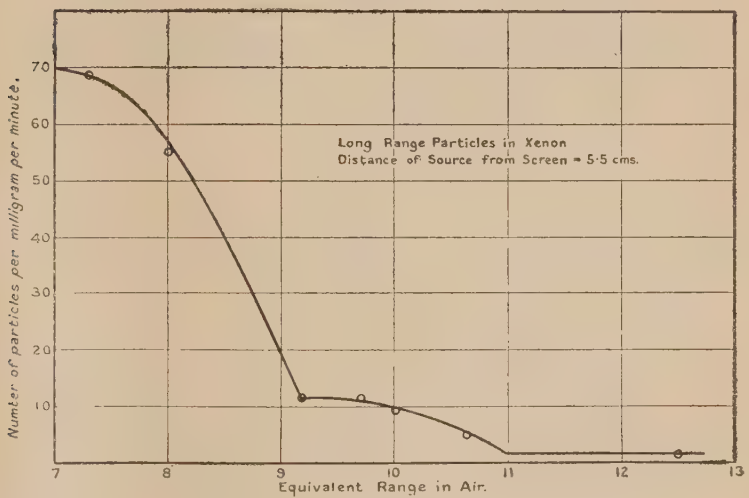
of the particles could be carried out with greater detail. The apparatus, shown in fig. 2, consisted of a brass tube 15 mm. in diameter, closed at one end by a glass plate carrying the ZnS screen, and having at the other end a brass slide which could be lowered in front of the source S by means of a winch. The distance between the source and screen was 5·5 cm. After introduction of the source, the apparatus was exhausted and then filled with xenon to a pressure of about 50 cm. of mercury. This was sufficient to absorb completely the α-rays of 7 cm. range. The number of scintillations observed on the screen was then counted at various increased pressures of xenon up to atmospheric pressure. For the highest absorptions a mica sheet was placed in front of the screen. In such cases it was arranged that the main α-particles were completely absorbed in xenon

and did not hit the mica, thus avoiding the production of extraneous H particles.

The occurrence of contamination could be at once detected by lowering the brass slide to cover the source. Some of the earlier experiments in xenon were completely vitiated by the presence of minute traces of radium emanation. As there is no satisfactory method of separating the emanation from xenon, the experiments had to be postponed until the emanation had decayed to a negligible amount.

The results of these experiments are shown in the curve of fig. 3, which gives the number of particles per minute

Fig. 3.



per mg. activity of the source at different absorptions, given in equivalent cm. of air. The curve shows clearly the existence of particles of two ranges, one just over 9 cm., the other about 11 cm. The number of particles of range greater than 11 cm. is very small, and there is no evidence of the group of 13·3 cm. range found by Bates and Rogers.

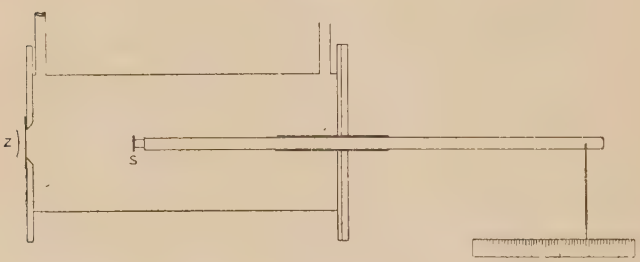
The area of the ZnS screen was 50 sq. mm., its efficiency about 70 per cent., and the distance from the source to the screen was 5·5 cm. We find therefore in xenon that 1 mg. of radium C emits about 1200 long-range particles per second, 1050 of a range of 9·3 cm. and 190 of a range of 11 cm.

A series of experiments was now carried out with the

source of α-rays surrounded by carbon dioxide. The arrangement will be clear from the diagram of fig. 4. The source was placed in a brass box, the face of which was provided with a hole covered with a sheet of mica of 1·9 cm. stopping power. Sheets of mica of known air equivalent could be introduced in the path of the long-range particles just in front of the ZnS screen. The distance of the source from the screen could be varied at will and measured on a scale outside the box. A slow stream of carbon dioxide was passed through the box during the experiments.

We again observed the particles of 9·3 range and in the same numbers as in previous experiments, but the main point of this experiment was to determine the number of 11 cm. particles and to search closely for the presence of others of longer range. For this purpose, the source was fixed at a distance of 4·6 cm. from the mica sheet covering

Fig. 4.



the hole in the face of the box, so that the main α-particles, of range 4·55 cm. in carbon dioxide, were completely absorbed in the gas.

The results of two typical experiments are shown in the curves of fig. 5. It will be seen that the number of 11 cm. particles is the same in both, the only difference being in the number of particles of longer range. There is no evidence whatever of a group of particles of range 13 cm. From these experiments we find that 1 mg. of radium C emits per second 180 particles of range 11·2 cm., in good agreement with the number found in xenon.

These particles were also examined when dry air was passed through the apparatus, the distance of the source being increased to 7·3 cm. The number of particles observed agreed with our previous results, but the observations were more difficult on account of the comparatively large number of particles which were present with ranges greater than 11 cm.

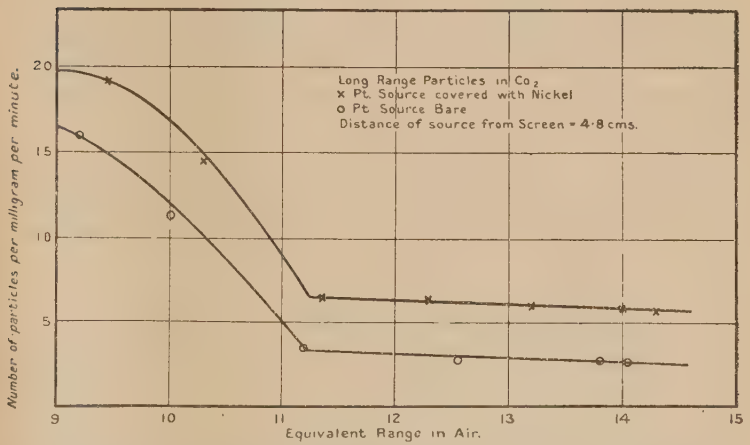
These were, of course, H particles due to the disintegration of nitrogen.

Further experiments were made in which the source of α-rays was covered with a thin sheet of solid material of an air equivalent of a few centimetres, the remainder of the range of the α-rays being absorbed in oxygen.

Using a thin sheet of silica of 2·3 cm. as absorbing material, we found that both the 9·3 and 11·2 cm. particles were present and in exactly the same numbers as in previous experiments. Very few particles were observed at greater ranges.

With a sheet of mica of 3·8 cm. stopping power, we observed the 9·3 cm. particles in their usual number. It was difficult

Fig. 5.



to measure accurately the number of 11 cm. particles against the background of H particles liberated from the mica by bombardment of the α-particles. These amounted to about 30 per cent. of the total number of particles of range greater than 7 cm.

Observations taken with a piece of copper foil over the source showed the great danger of using metal foils in work of this kind. The piece of foil was selected carefully and was used with a source of small area (3 mm. diameter) in order to minimise the risk of imperfections. In spite of these precautions it was found that the foil varied greatly in thickness. It was difficult, owing to the imperfections of the foil, to fix the end of the range of the α-rays with any accuracy, but it was evident that some parts of the foil had a stopping power of only 2·5 cm. of air, while the average

stopping power, deduced from its weight, was 3·8 cm. The result of these marked variations in thickness was to render the break between the main group of α-rays and the long-range particles far less obvious. With a uniform foil or in a gas, as in the experiments recorded above, the end of the range of the α-rays was extraordinarily definite and the presence of the long-range particles was brought out with great distinctness, while in this experiment with a copper foil there was merely a gradual diminution in the number of particles over a wide range of absorption. The failure of Fr. Dagmar Pettersson * to detect the long-range particles must be explained by such an effect of the imperfections of the foils used for absorbing the main α-rays.

The experiments described in this section show that when the α-rays are absorbed in helium, oxygen, xenon, carbon dioxide, silica, and mica, the long-range particles are always present. They consist of two groups, of equivalent ranges 9·3 cm. and 11·2 cm. The number of the 9·3 cm. particles emitted per second by a source of 1. mg. radium C is about 1050, the number of the 11·2 cm. particles about 180.

We conclude from these results that the number and range, in equivalent cm. of air, of these long-range particles are independent of the material in which the α-rays are absorbed.

§ 3. *Effect of different Methods of Preparation of the Source.*

The next point investigated was the influence of the method of preparing the source of radium active deposit on the number and range of the particles.

In the first place, observations with a source of pure radium C showed that it was this product, and not radium B, which gave rise to the long-range particles. On account of the greater ease in working, all other experiments were carried out with sources of radium B + C.

Usually the source of radium B + C was prepared by exposing a metal disk for about two hours to impure emanation. It was possible, though highly improbable, that the particles might be due to the disintegration of the metal or gases adsorbed in the metal. In most of the experiments described in the previous section the source was a platinum disk, which was heated to a high temperature in a vacuum furnace before exposure. Occasionally, brass and copper disks were used. The only difference noted was

* Dagmar Pettersson, 'Nature,' p. 641, May 3, 1924.

in the number of particles of range greater than 11 cm., which was less for the platinum source than for the others.

Sometimes, in order to minimise the risk of contamination, a thin film of copper or nickel was deposited electrolytically on the source. This had no effect on the number or equivalent range of particles.

Special sources were then prepared in the following ways. In the first method, a platinum foil was taken to a high temperature *in vacuo* for some hours and then exposed to purified emanation. In the second method, a piece of platinum foil similarly heated was suspended in a vacuum above a layer of emanation condensed by means of liquid air on the end of a glass tube. The active deposit was obtained on the platinum by recoil. This method is similar to that devised by Pettersson * for obtaining active sources.

In all these experiments the 9·3 cm. and the 11·2 cm. particles were always present and in the usual numbers, the only variation being in the number of particles observed at greater ranges (*cf.* the curves of fig. 5). The number of these was very small with a clean platinum source, particularly with sources prepared by the two later methods. They are probably due to traces of moisture in the material used to absorb the α-rays, or to moisture or possibly nitrogen adsorbed on the surface of the source.

We find, then, that the numbers and ranges of the long-range particles are independent of the method of preparation of the active deposit or of the material on which it is obtained.

§ 4. *The Origin of the Particles.*

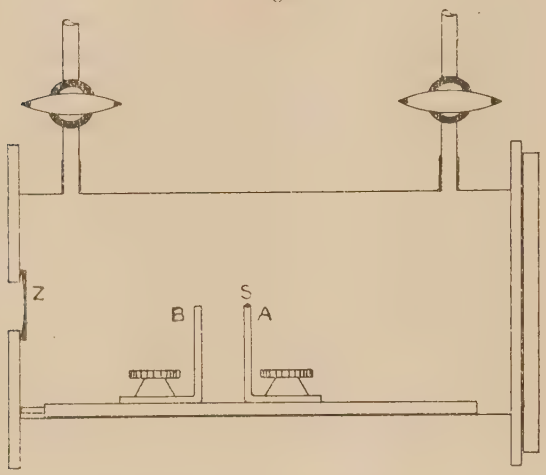
We shall now describe an experiment which shows that the long-range particles come from the source.

The apparatus is shown in fig. 6. The source, a platinum wire of ·25 mm. diameter, was carried in slots at A, and a graphite edge was placed 1 cm. distant at B. The zinc-sulphide screen, Z, was 5 cm. distant from the source. Carbon dioxide was circulated slowly through the apparatus. When the pressure of the gas was reduced sufficiently to allow the main α-rays to reach the screen, a sharp shadow of the graphite edge was formed. The position of the microscope was adjusted so that a cross-wire in the eyepiece coincided with this edge. The pressure of the gas was then restored to atmospheric, and the scintillations due to the long-range particles were observed. It was found that no

* Pettersson, *Wien. Ber.* 132. p. 55 (1923).

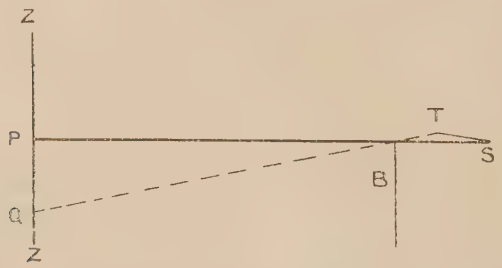
scintillations, except those due to the natural effect of the screen, occurred above the cross-wire, that is, below the edge of the shadow. This admits of two explanations.

Fig. 6.



Either the long-range particles are emitted from the source, or, if they arise in the gas, their direction of emission cannot make an angle of more than a few degrees with the direction of the impinging α-particle. This is made clear by the diagram of fig. 7, in which P is the shadow of the edge B given

Fig. 7.



by a beam of α-particles from the source S. If the long-range particles were produced in the gas and if their direction of emission made even a small angle with the direction, say ST,

of the colliding α-particle, then scintillations would be observed on the screen below P, for example at Q.

Taken in conjunction with other evidence, this experiment provides a simple and direct proof that the long-range particles are emitted by the radioactive matter of the source.

§ 5. *The Magnetic Deflexion of the Particles.*

In some unpublished experiments Bates and Rogers, by a method similar to that used by one of us for the same purpose, compared the magnetic deflexion of the 9·3 and 11·2 cm. particles with that shown under the same conditions by the α-rays of thorium C of 8·6 cm. range. Within the limits of error of the experiment, the results obtained were consistent with the view that both sets of particles were α-particles.

We have measured the magnetic deflexion of the 9·3 cm. particles by two methods.

In the first method, we used the arrangement described in the previous section, in which the particles pass through an atmosphere of carbon dioxide and throw a shadow of a graphite edge on the zinc-sulphide screen. If a strong magnetic field be applied at right angles to the path of the rays and to the plane of the diagram of fig. 6, the particles will be deflected and the shadow of the graphite edge will move downwards, say. On reversing the direction of the field, the shadow will move upwards. The distance between the two positions of the shadow gives a measure of the value of mv/e for the particles.

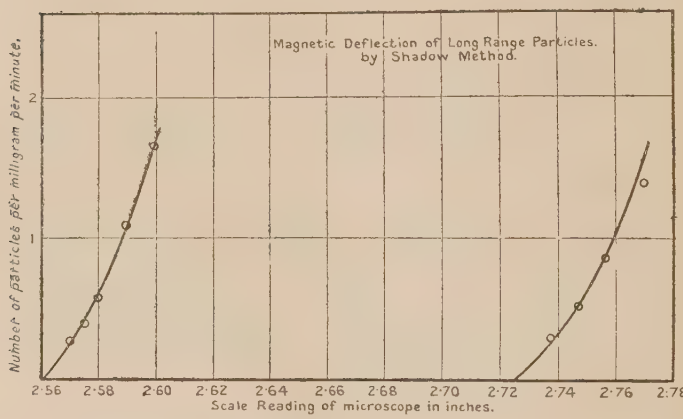
The apparatus was calibrated by observing the deflexion of the shadow cast by the α-particles of range 8·6 cm. emitted from a strong source of thorium B + C. The number of scintillations was so great as to give a definite edge to the beam, and the cross-wire of the microscope could be adjusted on the edge with great accuracy. With a current of 6 amps. through the magnet coils the distance between the two positions of the edge was ·173 inch or 4·39 mm.

The number of the 9·3 cm. particles was not sufficient to show at once the sharp edge of the shadow. For these particles, the microscope was set with the cross-wire close to the edge of the beam, and the number of particles appearing above the cross-wire was counted as the microscope was moved by successive small steps into the beam of particles.

The result of one experiment is shown in fig. 8. The ordinates give the numbers of particles counted above the cross-wire per mg. activity of the source for the different positions of the microscope given by the abscissæ. The point of intersection of the curve with the base-line gives the position of the edge of the shadow, and it is seen that this can be fixed with surprising accuracy.

A little consideration will show that the edge of the upper shadow is formed by the less deflected particles, the edge of the lower shadow by the more deflected particles. Thus only the readings of the upper edge are affected by the presence of the 11·2 cm. particles. This effect is not serious on account of the relatively small number of these particles.

Fig. 8.



The distance between the two positions of the edge found from the above experiment was ·165 inch. In a second experiment, we found a value of ·166 in., a rather better agreement than one would expect from the nature of the experiment.

Comparing this with the deflexion found for the α-particles of thorium C, and allowing for the difference in range, we see that the long-range particles have very closely the same value of mv/e as α-particles of the same range.

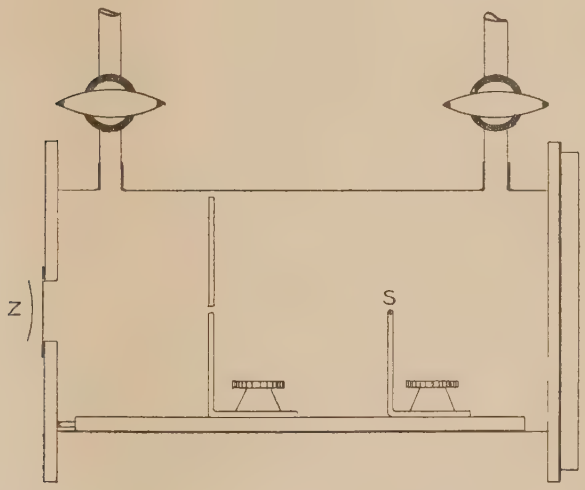
A further check can be obtained by measuring the magnetic field and calculating the deflexion which would be shown by an α-ray of range 9·3 cm. under the experimental conditions, *i.e.*, taking into account the change of velocity along the path through the gas. In this way we

find a deflexion of 4·23 mm., compared with the deflexion of 4·20 mm. observed for the long-range particles.

We conclude, therefore, that the long-range particles of 9·3 cm. range are α-particles.

The second arrangement for measuring the magnetic deflexion of the long-range particles is shown in fig. 9. It consists of a wire source of ·25 mm. diameter and a slit of ·5 mm. width contained in a narrow brass box. The box was evacuated during the experiments. The end of the box was closed by a brass plate containing a rectangular aperture 1½cm. × 1·5 cm., over which a mica sheet of 7·2 cm. air

Fig. 9.



equivalent was fixed. The ZnS screen was outside the box, and was fixed to the microscope, so that the same part of the screen was always observed. The distance from the source to the slit was 5 cm. and to the screen 10 cm. Under these conditions the width of the band of scintillations observed on the screen was 1·25 mm. The position of this band was observed when no magnetic field was applied and then with a field of about 12000 gauss, due to a current of 6 amps. through the magnet coils. A diaphragm of rectangular aperture and a central cross-wire were placed in the eyepiece of the microscope, giving a field of view 8 mm. in length and 1·54 mm. in width.

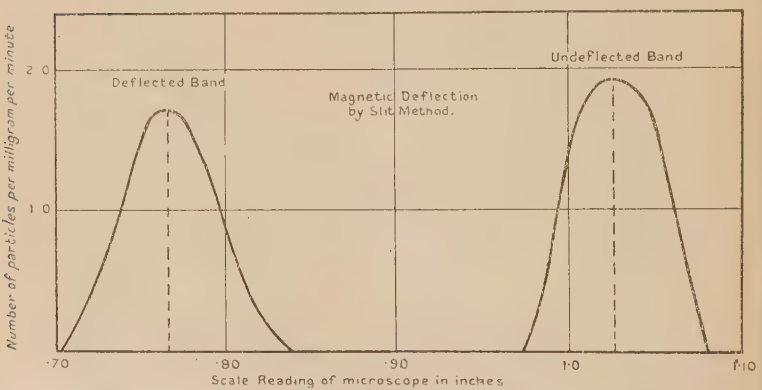
First, the deflexion of the α-rays of 8·6 cm. range emitted

by thorium C was examined, using a source of 1 mg. of thorium B + C. This gave a band of scintillations with sharp edges on which the cross-wire could be easily adjusted. With the magnetic field due to a current of 6 amps. the band was deflected through a distance of ·261 in. or 6·63 mm. This experiment also enabled us to fix accurately the centre of the undeflected band.

The source of radium B + C was then placed in position and scintillations were counted as the microscope was moved over the deflected band of long-range particles. The main α-rays of 7 cm. range were cut out by the mica. The position of the undeflected band was measured in a similar way.

The result of the experiment is shown in fig. 10. The

Fig. 10.



maximum of the deflected band is displaced by a distance of ·259 in. from the centre of the undeflected band. The deflexion calculated on the assumption that the 9·3 cm. particles are α-particles is ·254 in., about 2 per cent. less. Under the circumstances this is a very fair agreement, for we must remember that besides the 9·3 cm. particles there are also present the group of 11·2 cm. particles, and some H particles produced in the mica sheet by the 7 cm. α-rays. In other experiments we have found that the number of these H particles is about 30 per cent. of the number of 9·3 particles. The magnetic field used was not sufficiently strong to separate completely the bands of scintillations due to the 9·3 cm., the 11·2 cm., and these H particles, which latter will be produced where the 7 cm. particles strike the mica. It is clear, however, that the effect of these extraneous particles is to shift the maximum of the band towards the

side of greater deflexion, and a detailed calculation of the variation in number of the scintillations which should be observed at different parts of the band gives a result which agrees closely with experiment.

A further point is brought out in this experiment. If the 9·3 cm. particles were not emitted by the source but due to bombardment of atoms in the path of the α-rays, then the deflected band should be found where the 7 cm. particles strike the mica, that is, its centre should be at ·747 on our scale (*cf.* fig. 10). As this is not the case, we have a further proof that these particles are emitted by the source.

We may also compare the number of particles observed in this experiment, *i. e.* when all gases surrounding the source are removed, with the number we should expect from experiments in gases. Taking into account the fact that only one side of the wire source is effective and that of the total length of 9·5 mm., 2·5 mm. were shielded by the slots in which the wire is held, we find that the numbers correspond closely.

We conclude from these measurements of the magnetic deflexion of the 9·3 cm. particles that they are α-particles emitted from the source and that their number is the same when the source is in a vacuum as when surrounded by a gas.

§ 6. *Summary.*

In the series of experiments described in this paper we have obtained definite evidence about the nature and origin of the long-range particles which appear from a source of radium C. This evidence may be summarized as follows :—

(1) The particles of 9·3 cm. range appear in equal amount in helium, oxygen, carbon dioxide, and xenon.

The same is true for the particles of 11·2 cm. range, though on account of the small number of these the evidence is not so definite.

The experiments with helium appear to us to give conclusive evidence against the hypothesis that the particles arise from disintegration of the gas through which the α-particles pass. Whatever opinions may be held as to the stability of atomic nuclei, no one will lightly suppose that a helium nucleus is of no more than average stability.

We have found no evidence of the particles of 13·3 cm. range claimed by Bates and Rogers. The number of 11·2 cm. particles is also much less than they state. These discrepancies are probably due to the use in their experiments of absorbing foils of mica. This gives rise to comparatively large numbers of H particles and renders the detailed

investigation of the particles of greater range than the 9·3 cm. rays much more difficult.

(2) Both sets of particles were observed, and in the same numbers as before, when sheets of silica and mica were placed immediately over the source.

Experiments with an absorbing foil of copper have shown the great danger of using metal foils in work of this kind.

(3) The particles appear in the same number and with the same range in whatever way the source is prepared.

(4) By a shadow method, we have shown that the particles come from the source, or, if produced in the gas, travel in the direction of the impinging α-particle.

(5) The deflexion of the particles in a magnetic field corresponds within a small experimental error with that to be expected if they are α-particles emitted by the radioactive source.

(6) The magnetic deflexion in a vacuum shows definitely that the particles of 9·3 cm. range are emitted by the source. The number of the 11·2 cm. particles is too small for the application of this test.

(7) The particles of 9·3 cm. range appear in the usual number when the space surrounding the source is evacuated.

From this evidence there appears to us only one possible conclusion, namely, that the long-range particles are α-particles arising from the disintegration of radium C. In the case of the 9·3 cm. particles the evidence is overwhelming. On account of the small number of the particles of 11·2 cm. range the experiments cannot be carried out in such detail and the results are less conclusive, but there is no reason to doubt that they are of the same nature. These two groups of α-particles probably represent new types of disintegration of radium C, but any speculation about the mechanism which gives rise to them would be out of place in this paper, in which we have tried to confine ourselves to the narration of the bare experimental facts.

Our thanks are due to Mr. Hirst and Mr. Osgood for their assistance in counting, and to Mr. G. R. Crowe for his help in preparing the sources and arranging the experiments.

Cavendish Laboratory,
July, 1924.

LIII. *On the Output of Radiation from the Quartz Mercury Arc during the Period after first striking.* *By* B. D. H. Watters, *B.Sc., Physics Dept., Middlesex Hospital* *.

DURING a series of observations on the time taken by a mercury arc to reach a steady state, certain variations of output were noticed during the first few minutes.

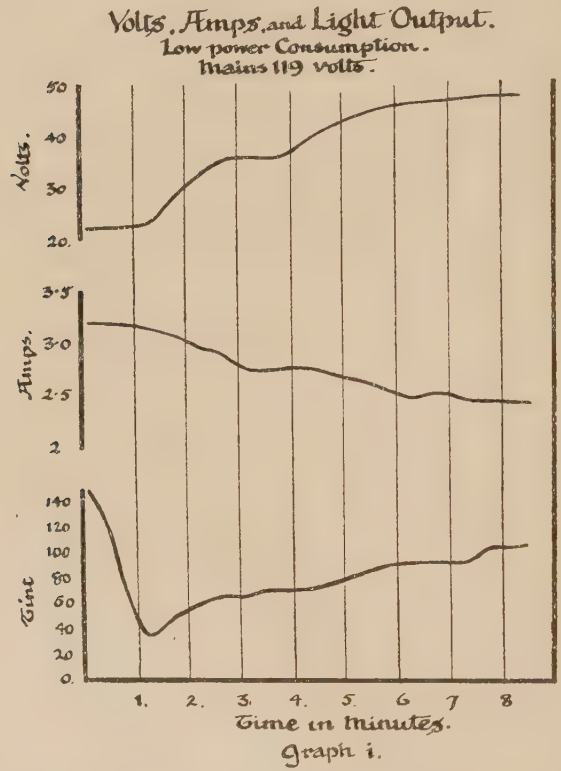
The rate of consumption of electrical energy by the lamp at any moment was measured by an ammeter placed in the circuit and a voltmeter across the lamp terminals, the current being drawn from a bank of accumulators to ensure steady supply conditions. The arc was then struck and readings of the instruments taken after 15 secs. and then at intervals of 30 secs. The output of light was measured by the tint obtained on a strip of gelatino-chloride printing paper (P.O.P.) exposed to the full radiation from the lamp behind an aperture. At the end of 30 secs. the strip was moved on sharply, any error introduced in the actual movement being much less than could be detected by the method of tint matching. In this way a series of tints was obtained, the depth of colour being a measure of the output during consecutive periods of 30 secs. It will be noticed that the reading of voltmeter and ammeter occurs at the mid point of each photographic exposure.

To obtain a relative figure expressing the depth of the tint the lamp was allowed to attain a steady state. When both instruments registered constant readings and the sensitive paper a constant tint, a series of standard tints was prepared on a piece of the same paper by exposing it for times ranging from 5 to 40 secs.

Each tint of an experimental series was then matched against the standard series and thus given a relative value. By this method the tints are expressed as a percentage of the tint corresponding to the final output, *i. e.* when the lamp has reached a steady state. An alternative method making use of a series of permanent standard tints made in water colours was tried, but the difficulty of colour matching and the additional error thus introduced confirmed the use of the simpler method described above. This method it will be noticed has also the advantage that any error due to variation in sensitivity and colour of one batch of printing paper from another is eliminated by using the same sheet for both exposures. The matching was done by the light of a 4-volt electric lamp kept at a constant distance.

* Communicated by Prof. Sidney Russ, D.Sc.

It was found that, whatever the experimental conditions of voltage and series resistance, the first tint was always deeper than those immediately following. This preliminary burst of light was followed by a fall to a minimum, and then a slow and rather jerky rise to a steady output which was attained in 10 to 15 minutes. The first effect is especially marked when the lamp is run at a low power consumption

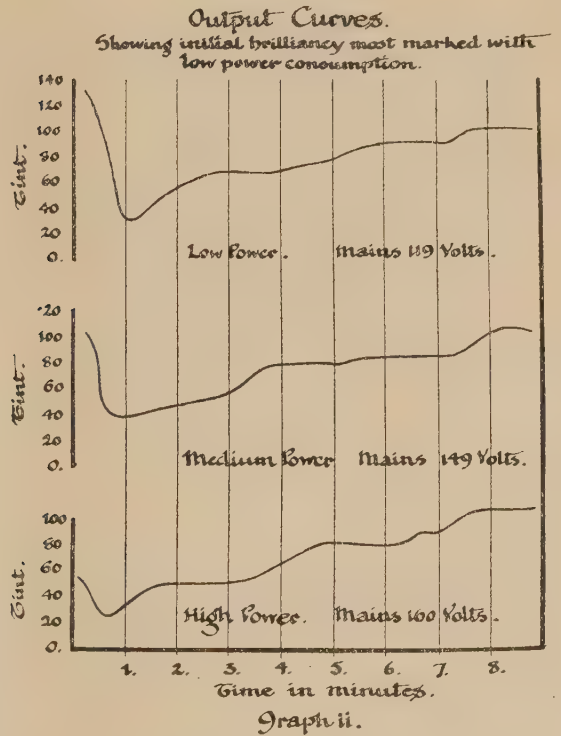


Graph i.

(see Graph II.). In one experiment (see Table I.), when the lamp was running at its lowest possible voltage, the output recorded by the sensitive paper during the first half-minute fell to a quarter of that value in the period following next but one. It will also be noticed from the table that the lamp did not regain the original intensity, the initial tint being about 40 per cent. deeper than the final steady output. The fluctuations in voltage, current, and tint output are shown

in Graph I., and it will be noticed that during the period of the rapid change in the intensity of the radiation, the readings of both instruments are virtually steady. On the other hand, the irregular rise in voltage and corresponding fall in current are roughly reflected in the output curve.

All these observations were made with the whole light from the arc. In order to discover whether the effect was confined to any particular part of the discharge, an apparatus

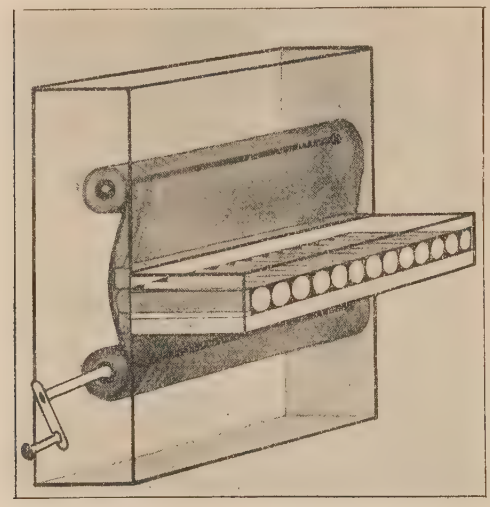


Graph ii.

was constructed, a sketch of which is shown in fig. 1. This apparatus consisted essentially of 11 lengths of brass tubing, each 7·5 cm. long and 1 cm. diameter, placed side by side in a frame and fixed in the front of a light-tight box. Inside the box was a simple mechanism by which a wide strip of sensitive paper was wound off one small roller on to another in such a way that it was stretched across the farther ends of the tubes. In order to minimise reflexions the inside surfaces

of the tubes were given a mat black coating of lamp-black and turpentine. The apparatus was adjusted close up against the lamp, so that each tube received the light from a small section of the tube only. When this strip was exposed for consecutive 30-second intervals after striking the arc, the

Fig. 1.

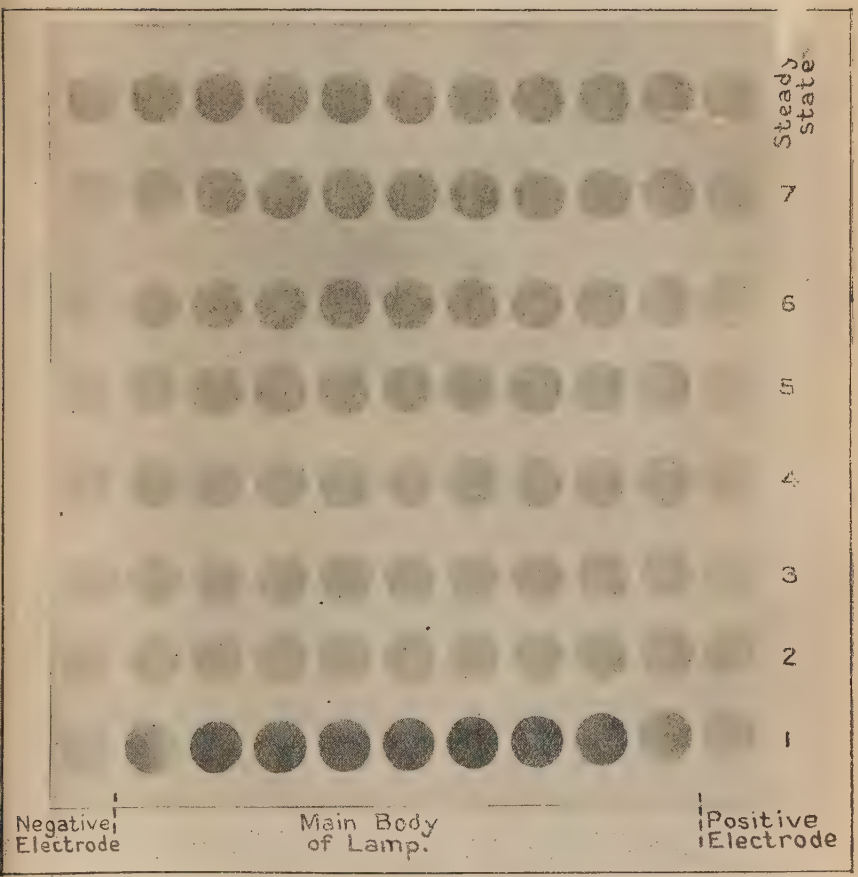


result shown in fig. 2 was obtained. The bottom line of tints is the first exposure. The first tube on the right was bearing on the positive electrode, the large spherical bulb which remains about half full of mercury. Owing to the low voltage at which the lamp was run, the discharge does not fill the bulb, which is, therefore, not very brilliant. The negative electrode is covered by the tube on the extreme left and the main body of the lamp by the nine central tubes. The print shown is typical of a number obtained in this way, and shows clearly that the initial brilliance is confined to the centre portion of the tube, there being no trace of it at either electrode.

A spectroscopic examination of the radiation was then made, using a Hilger quartz spectroscope and panchromatic plates. The same exposure period of half-a-minute was employed, the light being taken from the centre of the lamp only, making use of the apparatus described above. On each

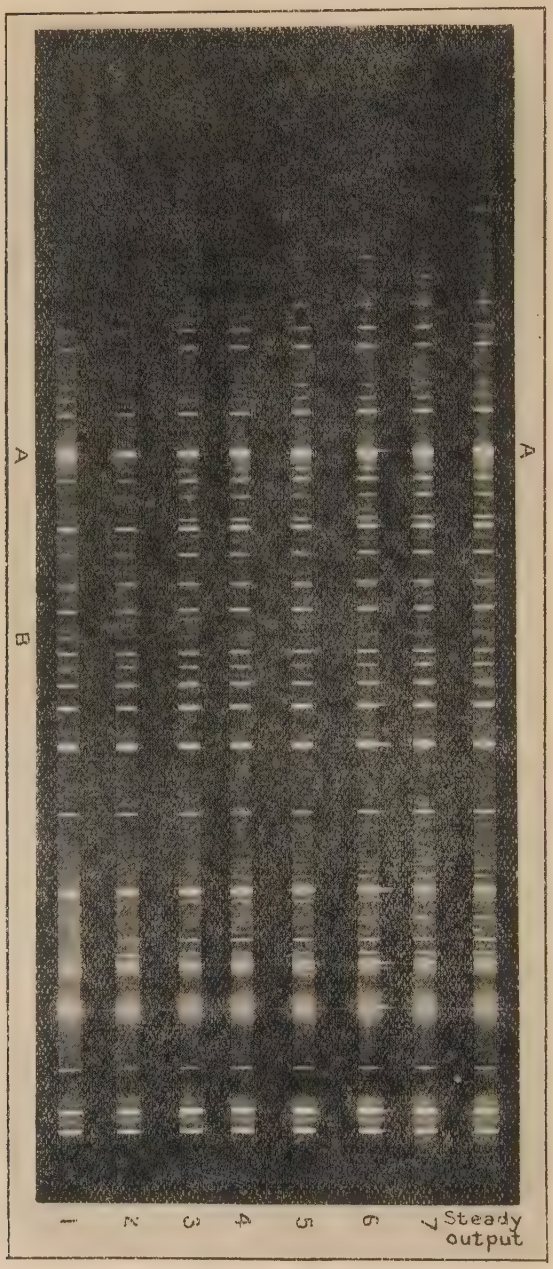
plate the spectrum of the steady radiation was also included for purposes of comparison.

Fig. 2.



A typical result is shown in fig. 3. The first spectrum is the lowest on the plate, and it will be seen that it is very much simpler than the top one which is the spectrum of the steady state. A number of the lesser lines do not appear at all until after a minute or more has elapsed. Some lines show, on the other hand, a marked maximum at the start, followed by a sharp drop, and then a steady increase. The less intense lines of this type fade away entirely and reappear

Fig. 3.



again. The most marked example is the line of wave-length (λ 2536), which is marked A in the print. There can be little doubt that it is this line which is responsible for the effect under observation. It is interesting to note that in some earlier experiments this line was found to have by far the greatest photoelectric effect of all the lines of the mercury spectrum *. The initial brilliance was somewhat exaggerated by the selectivity of the paper. It was found that this paper was sensitive throughout the whole range of the ultra-violet covered by the quartz spectrometer.

A print was made in the spectroscope directly on the paper by an exposure of over four hours, which showed that the yellow and green lines had little or no effect, whilst all the main lines in the ultra-violet were strongly marked. The selectivity of the printing paper thus accentuates any fluctuation in the ultra-violet region.

An attempt was made to record the fluctuations during periods of about 1 sec. A revolving shutter with a sector of 180° was used, but beyond confirming the fact that the intensity of λ 2536 starts at a maximum value at the instant of striking the arc, nothing very conclusive could be obtained.

To measure any minor variation in intensity apparatus of precision would have been a necessity.

In order to summarise the evidence of the spectroscopic experiments, the lines may be divided into three groups. First, the lines which show a small but gradual increase of intensity as the lamp runs steady. Secondly, the lines which show an initial maximum followed by a drop and a steady rise. Thirdly, those which do not appear at all until an interval after the arc is struck. One minor line cannot be placed under any of these categories. This line (λ 2848), marked B in fig. 3, appears only in the Starting Spectrum for the first 30 secs., and cannot be detected in any of the subsequent exposures.

With the object of discovering whether this phenomenon was peculiar to the mercury arc, similar experiments were made with a number of metallic arcs in air. Owing, however, to the unsteady running, during the essential early stages, nothing very conclusive was obtained except that in the case of the iron-arc an undoubted starting maximum was obtained for every condition of voltage and current employed.

* Clark and Watters, Jour. Röntg. Soc. xvii. July 1922.

TABLE I.

Energy Consumption and Radiation output of a mercury lamp. Low mains voltage 119 volts.

	Time.	Volts.	Amps.	Watts.	Tint %.
1	0.15	22	3·2	70	133
2	0.45	22	3·2	70	73
3	1.15	23	3·15	70	33
4	1.45	24	3·1	74	50
5	2.15	28	2·95	82	60
6	2.45	32	2·9	93	66
7	3.15	35	2·75	96	66
8	3.45	35	2·75	96	70
9	4.15	35	2·75	95	70
10	4.45	38	2·7	103	75
11	5.15	41	2·6	107	80
12	5.45	43	2·55	109	87
13	6.15	44	2·45	108	90
14	6.45	45	2·45	110	90
15	7.15	45	2·5	112	90
16	7.45	46	2·45	110	100
17	8.15	47	2·4	110	100
18	8.45	47	2·4	110	100
19	9.15	47	2·4	110	100
20	9.45	47	2·4	110	100
--	—	—	—	—	—
-	—	—	—	—	—
30	15.15	48	2·3	110	100

TABLE II.

Showing variation of output after striking the arc under different voltages.

Time.	Low Power. (Mains 119.)	Medium Power. (Mains 149.)	High Power. (Mains 160.)
0.15	133	100	45
0.45	73	40	25
1.15	33	40	40
1.45	50	45	45
2.15	60	47	45
2.45	66	50	47
3.15	66	60	50
3.45	70	75	60
4.15	70	75	70
4.45	75	75	75
5.15	80	75	75
5.45	87	80	75
6.15	90	80	75
6.45	90	80	85
7.15	90	90	90
7.45	100	100	100
8.15	100	100	100
8.45	100	100	100

Note that the tints are all expressed as percentages of the final steady condition for that experiment. With the higher mains voltage, the final output is greater and the tint therefore deeper than the corresponding tint obtained with a lower voltage. The final tints are in the ratio approximately 35 : 65 : 100.

LIV. *An Electrical Method for Tracing Stream Lines in the Two-Dimensional Motion of a Perfect Fluid. By* E. F. Relf, *A.R.C.Sc., of the Aerodynamics Department, National Physical Laboratory* *.

IT has long been known that the equations giving (for two-dimensional systems) the stream lines in a non-viscous fluid and the equipotential lines in an electric field are identical. In both problems the equation

$$\nabla^2\psi = 0$$

must be solved subject to the condition that ψ has a constant value over every boundary, the actual values of ψ at the different boundaries depending upon the nature of the problem. The two-dimensional flow of a perfect fluid passing an obstacle such as an aerofoil can, therefore, be conveniently mapped if a suitable method can be found for tracing the system of equipotential lines due to a metal aerofoil placed in an electrostatic field. This field may be produced between two parallel metal plates, and the solution obtained is then equivalent to that of fluid flow past the obstacle and between parallel walls. The solution is practically unaffected when the dielectric between the plates is replaced by a substance of very low conductivity.

The apparatus described below was designed and constructed for use in the Aerodynamics Department of the National Physical Laboratory, in order that stream lines round an obstacle might be rapidly and accurately plotted in this way. A photograph of the apparatus is given in fig. 1. It consists of a concrete tank, 5 ft. long, 2 ft. 6 in. wide and 1 ft. 3 in. deep, filled with ordinary tap-water and coated inside with bitumastic enamel to prevent absorption of the water by the concrete. On the two longer sides are mounted thin sheets of aluminium, and the metal model of the obstacle to be studied stands in the centre of the tank.

The use of a steady potential difference between the two side plates leads to electrolytic troubles, and was abandoned in favour of an alternating potential difference of audible frequency, a telephone being used as an indicator. The resistance of the water between the plates is of the order of 100 ohms.

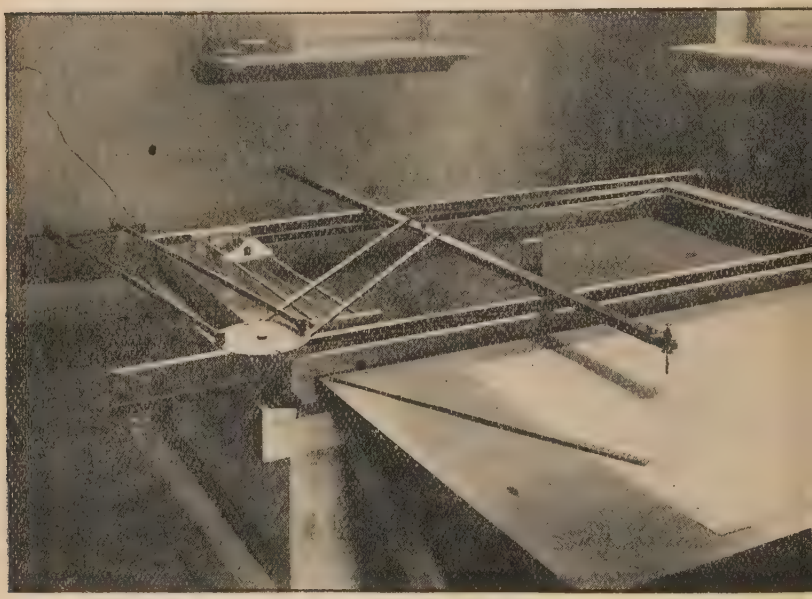
To determine the equipotential lines two exploring electrodes are used, consisting of fine platinum wires sealed into the ends of capillary tubes and projecting about 1/10 in. from the ends. One of these electrodes is fixed at any

* Communicated by Mr. R. V. Southwell.

convenient point in the tank, while the other is carried on a pantograph of the drafting-machine type. This pantograph also carries a steel point, which copies exactly the motion of the exploring electrode over a drawing-board placed beside the tank.

The alternating potential difference is obtained from an oscillatory valve circuit in which the secondary and primary windings of an ordinary low-frequency inter-valve transformer are used in the plate and grid circuits respectively.

Fig. 1.

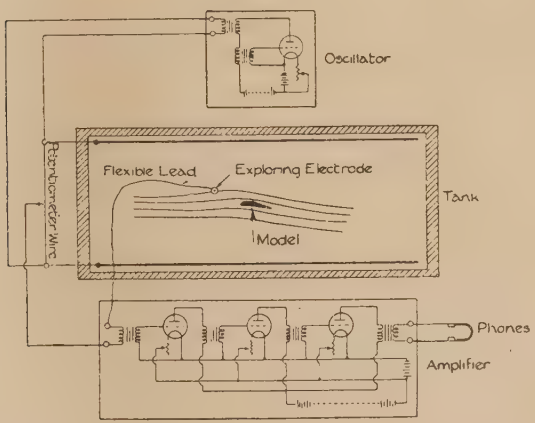


This circuit was found to oscillate at about 200 per sec frequency without the introduction of any capacity across the winding in the plate circuit, and gives a very constant and pure tone. The two exploring electrodes are connected to a three-valve low-frequency amplifier. A diagrammatic sketch of the apparatus, showing the electrical circuits, is given in fig. 2. The observer listens in the headphones connected to the output side of the amplifier, and adjusts the movable electrode until no sound is heard. The two electrodes are now at the same potential, and a mark is made by depressing the steel point on the pantograph so that it makes

a pin-prick in a sheet of paper fixed to the drawing-board. The process is repeated until sufficient points have been obtained to define the equipotential line passing through the fixed electrode. This electrode is then moved to a new position and another line drawn in the same way, and so on until the whole field is mapped. The process is very rapid in practice, and under good conditions the position of the movable electrode is determinable within about 1/100 in.

If it is desired to know the spacing between the equipotentials expressed as a fraction of the potential difference between the plates, a fine potentiometer wire is connected

Fig. 2.



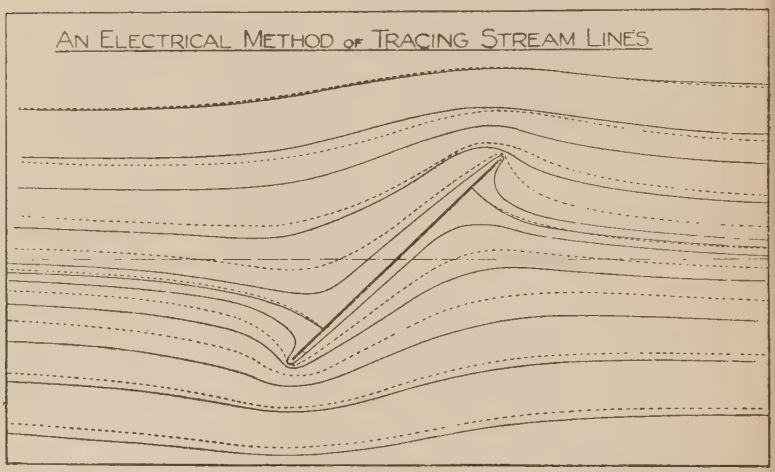
between the plates and points on this wire are employed to give reference potentials instead of the fixed electrode.

Used in the above way the apparatus will draw the stream lines of an inviscid fluid without circulation, because, since the model is insulated, the total electric flow across its boundary must be zero. The case in which circulation is present may be obtained by connecting the model to a point on the potentiometer wire, so that it is at a potential different from that which it would assume if insulated. In practice this method has not been used, on account of the difficulty of measuring the potential of the model, or the current flowing into it, in order to define the amount of circulation. Instead, the stream lines due to circulation alone are mapped by connecting both the side plates to one side of the alternating supply and the model to the other side, the potentiometer wire being used as before to supply the

reference potentials. The flow due to circulation of any desired magnitude can then be added graphically to that for non-circulatory flow.

Two illustrations of the results obtained with the above apparatus are appended, and problems were chosen for this purpose in which a direct comparison with theory was possible. The first of these (fig. 3) gives the stream lines for non-circulatory flow past a flat plate inclined at 45° to the direction of flow. The full lines were obtained by the electrical method, whilst the dotted lines were obtained from the hydro-dynamical equations. No attempt was made to measure the values of ψ for the various stream lines, and the comparison is accordingly to be made on the basis of the

Fig. 3.



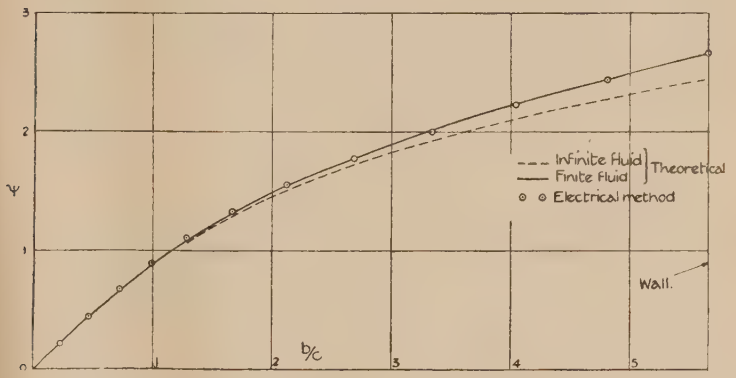
conformity of the two sets of stream lines. It will be noted that the two sets of lines agree remarkably well, even near the sharp edges of the plate, where the curvature is greatest.

The second illustration was obtained from measurements of the stream lines due to circulation only round the same flat plate. In this case the potentiometer wire was used as a reference, and it is possible to compare the actual values of ψ. This is done in fig. 4, which relates to the distribution of ψ along an axis bisecting the width of the plate at right angles. In an infinite fluid the stream lines for the flat plate are confocal ellipses with foci at the edges of the plate *, and the dotted curve gives the values of ψ along the above line (*i. e.*, along the minor axes of the ellipses) for various values of b/c, b being the distance from

* Lamb, 'Hydrodynamics' (3rd edition), § 66.

the flat plate and $2c$ the width of the plate. It was realized that the effect of the walls of the tank would not be negligible, excepting in the region very near the plate, and its effect upon the values of ψ along the chosen line was calculated by the method of images. This gave the full curve of figure 4. The points on the same diagram were obtained by direct measurement from the stream lines traced by the electrical method, the arbitrary scale of ψ (as given by the potentiometer wire) being so chosen as to make the potential at the side plates correspond with the calculated value of ψ (allowing for wall interference) at this distance from the plate. It will be seen that the agreement is very good indeed. It was noticed that although the presence of the

Fig . 4.



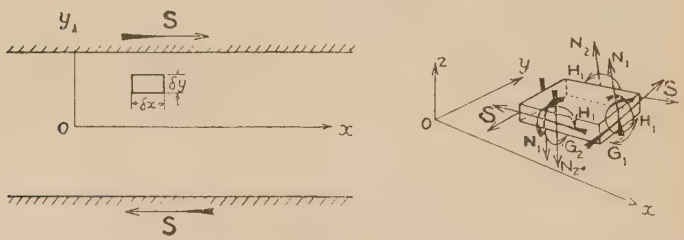
walls modifies considerably the values of ψ far from the plate, yet the stream lines, when plotted from the electrical determination, would be judged to be coincident with the system of ellipses given by theory for an infinite fluid. In other words, the change of shape of a given stream line which is produced by the introduction of the wall interference is not striking to the eye, although the actual value of ψ at a given point has been considerably altered. This fact serves to explain the agreement in the shape of the outer stream lines of fig. 3, where the comparison is with theoretical lines for an infinite fluid.

The apparatus is thus demonstrated to be sufficiently accurate for practical purposes, and it provides a very convenient and rapid method of solution of the stream-line problem in two-dimensional cases which can be conveniently represented in the electrical analogue.

LV. *Note on the Stability of Laminar Shearing Motion in a Viscous Incompressible Fluid.* *By* R. V. Southwell, *M.A., Superintendent of the Aerodynamics Department, National Physical Laboratory* *.

1. In collaboration with Miss S. W. Skan †, I have recently investigated the effects of applied shearing forces upon the free transverse vibrations of a flat elastic strip. Fig. 1 shows the nature of the problem and the notation which was employed. To avoid unnecessary complication arising out of end effects, the length of the strip was taken as infinite and the transverse displacement assumed to be simply harmonic in x: under these conditions no restriction is imposed upon the wave-length of the displacement in a direction parallel to the edges, and the results were accordingly presented in diagrams which related the natural frequency of vibration with this wave-length and with the intensity of the applied shearing forces.

Fig. 1.



Two types of edge constraint were considered, namely, "simple support" and "clamping." The first type prevents displacement of the middle-surface at the edges, which are otherwise free; the second also prevents change of slope at the edges. The diagram corresponding to the second conditions is reproduced as fig. 2 of the present note: abscissæ are values of the ratio l/b, where l is the wave-length of the displacement and b the half-breadth of the strip; ordinates are values of b^2S/D (denoted by the symbol A), where S is the intensity of the applied shearing forces per unit length of edge, and D is the "flexural rigidity" of the strip ‡: and

* Paper read at the International Congress for Applied Mechanics, Delft, 1924. Communicated by the Author.

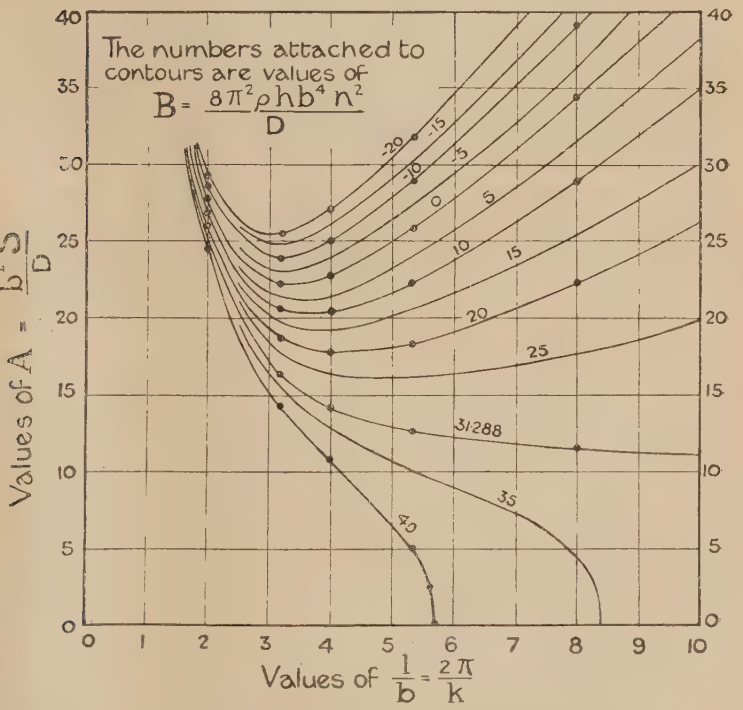
† Roy. Soc. Proc. A, cv. pp. 582–607 (1924).

‡ $D=2Eh^3/3(1-\sigma^2)$, where h is the half-thickness of the strip, E is Young's modulus, and σ is Poisson's ratio. *Cf.* §2 of the paper cited.

the curves shown are contours drawn for constant values of the quantity $8\pi^2\rho hb^4n^2/D$, where n is the frequency of the transverse vibrations, ρ the density and h the half-thickness of the strip. Thus all the quantities which occur in fig. 2 are non-dimensional, and any consistent system of units may be employed.

It is evident from this diagram that an increase in the intensity of shear, for any definite value of the wave-length,

Fig. 2.



will be accompanied by a decrease in the value of n^2. At some particular value of S (corresponding to the contour numbered 0) the period of vibration becomes infinite and the distorted form can be maintained indefinitely, the elastic stability of the system being then neutral; whilst if S be increased beyond this value, n^2 becomes negative, and the vibrations are characterized by an imaginary period,—*i. e.*, the system becomes elastically unstable, and the transverse displacements increase (or decrease) exponentially in respect of time.

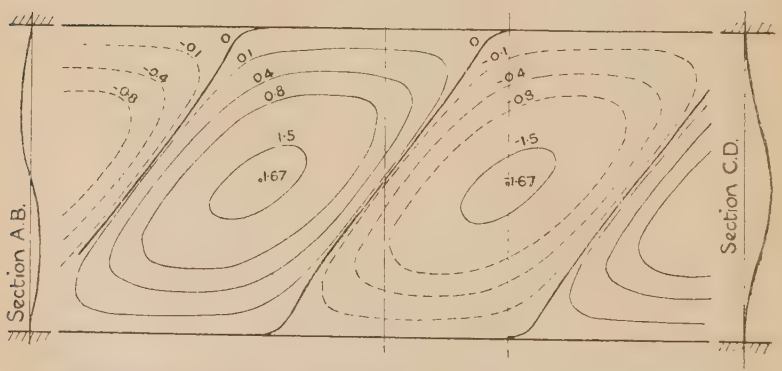
It is more natural to treat S or n as the specified quantity, since in reality, as was remarked above, no restriction is imposed upon the value of the wave-length. The diagram shows that in the absence of applied shear ($A=0$) the gravest frequency of vibration corresponds to a displacement of two-dimensional type ($l=\infty$), but that when S has a finite value the gravest frequency corresponds to a displacement having a finite wave-length; conversely, among vibrations having a specified frequency there is some one type, characterized by a finite wave-length, which requires a smaller shear than any other for its maintenance.

From a practical point of view, the most important conditions are those of neutral elastic stability, corresponding to the contour numbered 0 in fig. 2. Our calculations showed that the smallest shear required to produce these conditions, in a strip of which the edges are clamped, is given by

$$\frac{b^2S}{D} = 22{\cdot}18, \text{ approximately, } . \quad . \quad (1)$$

and that the corresponding displacement has a wave-length about 1·6 times the breadth of the strip*. It was thought

Fig. 3.



worth while to investigate the nature of the displacement in some detail, since experimental results could easily be obtained for comparison†, and a series of contours of constant displacement was accordingly plotted in a diagram which is reproduced as fig. 3 of the present note. The numbers attached to the contours have a relative significance

* *Cf.* Table II. of the paper cited.

† A specimen strip, from a series tested in the Engineering Department of the National Physical Laboratory, was lent by Mr. H. Gough for reproduction (as part of fig. 1) in the paper cited.

only, the absolute magnitude of the displacement being indeterminate.

2. There is no direct connexion, either physical or mathematical, between the problem of elastic stability here treated and that of the stability of laminar shearing motion in a viscous fluid; but it is the purpose of the present note to show that results of the type given in equation (1) above have an application to the hydrodynamic problem. From (1), for example, we can at once deduce a result which has been previously obtained by W. M. Orr *, whose formulation of the hydrodynamic problem has been accepted by Rayleigh † and H. Lamb ‡, and will be followed here.

3. The equation which governs the vorticity of a viscous fluid moving in two dimensions is

$$\frac{\partial \zeta}{\partial t} + u\frac{\partial \zeta}{\partial x} + v\frac{\partial \zeta}{\partial y} = \nu \nabla^2 \zeta, \quad . \quad . \quad . \quad . \quad (2)$$

where ν is the kinematic viscosity and $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2$. The vorticity

$$\zeta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where u and v are the component velocities of the fluid in the directions of x and y respectively.

In the case of uniform shearing motion between parallel planes $y=0$ and $y=d$, the former of which is at rest, we have in the undisturbed motion

$$u = \beta y, \quad v = 0, \quad \zeta = -\beta, \quad . \quad . \quad . \quad (4)$$

where β is a constant. For the disturbed motion we may write

$$u = \beta y - \frac{\partial \psi}{\partial y}, \quad v = \frac{\partial \psi}{\partial x}, \quad \zeta = -\beta + \nabla^2 \psi, \quad . \quad (5)$$

where ψ is the stream-function of the disturbance. Then *if the disturbance is infinitesimal* (so that terms of the second order in ψ may be neglected) we have, on substituting from (5) in (2),

$$\left[\frac{\partial}{\partial t} + \beta y \frac{\partial}{\partial x} - \nu \nabla^2\right] \nabla^2 \psi = 0. \quad . \quad . \quad . \quad (6)$$

* Proc. Roy. Irish Acad. xxvii. pp. 69–138 (1907).

† Phil. Mag. xxviii. pp. 609–619 (1914), or 'Collected Papers', vi. pp. 266–276. The notation employed in this note is substantially that of Rayleigh.

‡ 'Hydrodynamics', 3rd Ed. § 368. ζ as defined by Lamb (and in the treatment here given) has twice its value as defined by Rayleigh, and is of opposite sign.

This equation must be satisfied by ψ at every point in the fluid field, whilst the condition of "no slipping at solid boundaries" requires that

$$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial y} = 0, \text{ when } y = 0 \text{ and when } y = d. \quad . \quad (7)$$

In seeking to determine the conditions (if any exist) under which an accidental disturbance of the steady motion will tend to persist or to increase, we must ensure that such persistence is not in reality an effect of suitably varying pressure differences, implied in our solution, at the *ends* of the fluid field. This will be done if we make an assumption exactly similar to what was made for the elastic problem in § 1 above, and take the length of the fluid field to be infinite and the disturbance to be simply harmonic in x: our problem then becomes a limiting case of the problem of shearing motion between two concentric cylinders*, in which the radii of the cylinders are infinite. We therefore suppose that u, v and ζ, in so far as they depend upon x and t, are proportional to $e^{int}e^{ikx}$, where $n=p+iq$; and equations (6) and (7) then take the forms

$$\left[\frac{\partial^2}{\partial y^2} - k^2 + \frac{q}{\nu} - \frac{i}{\nu}(p + k\beta y)\right] \mathrm{S} = 0, \quad . \quad . \quad (8)$$

$$\text{where } \mathrm{S} = \nabla^2\psi = \left[\frac{\partial^2}{\partial y^2} - k^2\right]\psi,$$

and

$$\psi = \frac{\partial \psi}{\partial y} = 0, \text{ when } y = 0 \text{ and when } y = d. \quad . \quad (9)$$

The question of the stability of the steady shearing motion now turns on the sign of q in a disturbance of the type considered. If a solution of equations (8) and (9) can be found in which q has a zero or negative value, the steady motion will be neutral or unstable: if q is necessarily positive, the steady motion will be stable. The result due to Orr, of which mention has been made in § 2, is that no failure of the stability can occur unless the "Reynolds' number" $\beta d^2/\nu$ exceeds 177, where d is the distance between the walls, so that βd represents their relative velocity. Whether failure

* This problem has been investigated, both analytically and experimentally, by G. I. Taylor (Phil. Trans. Roy. Soc. A, ccxxiii. pp. 289–343, 1923), who has determined definite criteria of instability. The type of disturbance which is found to persist is, however, three-dimensional: it has no counterpart in the present problem.

can occur at some higher value of $\beta d^2/\nu$ is a question which does not appear to have received a completely satisfactory answer, in spite of the skilful treatment which the problem has received from many workers*: the general opinion seems to be that the steady shearing motion is completely stable for infinitesimal disturbances, but that the stability probably fails for finite disturbances, or (what is practically the same thing) when the walls are roughened by excrescences of finite size, if the Reynolds' number is sufficiently high.

4. To show that Orr's result can be obtained from the result for the elastic strip which has been stated in equation (1), we first consider the real form of the solution to (8) and (9) which corresponds to the symbolic form assumed in § 3. This may be written as

$$\psi = e^{-qt}\{\Psi_1 \sin(kx+pt) + \Psi_2 \cos(kx+pt)\}, \quad . \quad (10)$$

where Ψ_1 and Ψ_2 are functions of y only, such that

$$\Psi_1 = \Psi_2 = \frac{d\Psi_1}{dy} = \frac{d\Psi_2}{dy} = 0, \text{ when } y=0 \text{ and when } y=d, \quad (11)$$

and

$$\left.\begin{aligned} [q+\nu\nabla_1^2]\nabla_1^2\Psi_1 + (p+k\beta y)\nabla_1^2\Psi_2 &= 0, \\ [q+\nu\nabla_1^2]\nabla_1^2\Psi_2 - (p+k\beta y)\nabla_1^2\Psi_1 &= 0, \end{aligned}\right\} \quad . \quad (12)$$

where $\nabla_1^2 \equiv d^2/dy^2 - k^2$, at all points in the fluid field.

It is easily verified by substitution that (10) is a solution of (6) and (7). If we now multiply the first of (12) by Ψ_1 and the second by Ψ_2, add, and integrate between the limits $y=0$ and $y=d$, we have, in virtue of the boundary conditions (11),

$$\begin{aligned} \nu \int \{\Psi_1''^2 + \Psi_2''^2 + 2k^2(\Psi_1'^2 + \Psi_2'^2) + k^4(\Psi_1^2 + \Psi_2^2)\}\, dy \\ - q\int \{\Psi_1'^2 + \Psi_2'^2 + k^2(\Psi_1^2 + \Psi_2^2)\}\, dy \\ - k\beta \int (\Psi_1\Psi_2' - \Psi_2\Psi_1')\, dy = 0. \quad . \quad . \quad . \quad (13) \end{aligned}$$

Dashes here denote differentiation with respect to y.

5. We next consider the problem of a long flat strip in neutral elastic stability under the combined action (i) of a uniform shearing force, of intensity S per unit length, applied at its edges (exactly as in § 1) and (ii) of a uniform tension, of intensity T per unit length, acting in all directions in its plane. It can be shown† that the equation

* References have been given by Rayleigh and Taylor in the papers cited.

† *Cf.* §§ 8 and 19 of the paper cited above. The axes and notation have been explained in § 1 of the present note.

which governs the transverse displacement w of points in the middle surface is

$$D\nabla^4 w - 2S\frac{\partial^2 w}{\partial x\,\partial y} - T\nabla^2 w = 0, \quad . \quad . \quad . \quad (14)$$

and hence the elastic stability of the system will be neutral if a solution of (14) exists which is simply harmonic in x (*cf.* § 1) and which satisfies the appropriate boundary conditions. When the edges are clamped, these are

$$w = \frac{\partial w}{\partial y} = 0, \text{ at the edges of the strip. } . \quad . \quad (15)$$

Suppose that a solution of this nature exists, and let it be represented by the expression

$$w = W_1 \sin kx - W_2 \cos kx, \quad . \quad . \quad . \quad (16)$$

where W_1 and W_2 are functions of y only, such that

$$W_1 = W_2 = \frac{dW_1}{dy} = \frac{dW_2}{dy} = 0, \text{ at the edges of the strip.} \quad (17)$$

Then from (14) we have the equations

$$\left.\begin{aligned} [-T + D\nabla_1^2]\nabla_1^2 W_1 - 2kS\frac{dW_2}{dy} = 0, \\ [-T + D\nabla_1^2]\nabla_1^2 W_2 + 2kS\frac{dW_1}{dy} = 0, \end{aligned}\right\} \quad . \quad . \quad (18)$$

and if we multiply the first of (18) by W_1 and the second by W_2, add, and integrate over the breadth of the strip, we obtain, in virtue of the boundary conditions (17),

$$\begin{aligned} D\int \{W_1''^2 + W_2''^2 + 2k^2(W_1'^2 + W_2'^2) + k^4(W_1^2 + W_2^2)\}\,dy \\ + T\int \{W_1'^2 + W_2'^2 + k^2(W_1^2 + W_2^2)\}\,dy \\ - 2kS\int (W_1 W_2' - W_2 W_1')\,dy = 0. \quad . \quad . \quad (19) \end{aligned}$$

Dashes again denote differentiation with respect to y.

6. Equation (19) is the energy equation for the bent strip, expressing the condition that the work done by shear and tension, on the occurrence of the displacement w, is equal to the strain-energy stored by flexure. Now it has been shown

by Rayleigh * that, in problems of the kind which we are considering, an approximate expression for the gravest natural frequency of vibration may be obtained directly from the energy equation, if we assume for the type of the displacement any reasonable form which satisfies the imposed boundary conditions; and further, that if the assumed type is not an exact solution of the differential equation of motion the result of the determination will err in the direction of *overestimating the stability of the system*. Thus in particular, if we use his method to determine the conditions of limiting elastic stability (zero frequency), we shall overestimate the magnitude of the disturbing forces required, unless the assumed displacement is an exact solution of the equation of neutral equilibrium.

Let us apply his method in this way to the elastic strip, and let us suppose further that the quantities which defined this problem in § 5 are related with those of the hydrodynamic problem of §§ 3 and 4 by the scheme

$$\left.\begin{aligned} \mathrm{D} &= \nu, \\ -\mathrm{T} &= q, \\ \mathrm{S} &= \tfrac{1}{2}\beta, \\ 2b &= \text{breadth of elastic strip} \\ &= d. \end{aligned}\right\} \quad . \quad . \quad . \quad (20)$$

Then if, as our assumption in regard to the type of the displacement, we identify W_1 and W_2, in (16), with the functions Ψ_1 and Ψ_2 of § 4, the relation (19) becomes identical with (13), and is therefore satisfied. But the equations (18) cannot be identified with (12), and hence our assumed type does not satisfy (14) exactly: it follows, by the theorem quoted above, that we shall overestimate the shear (or the thrust, if q is positive) required to bring about conditions of limiting elastic stability.

7. Now it was shown in the paper cited † that correct relations between shear, thrust (or tension) and flexural rigidity, under conditions of neutral elastic stability, can be obtained from the diagram reproduced in fig. 2 above. The necessary calculations have since been made ‡, and are described in the

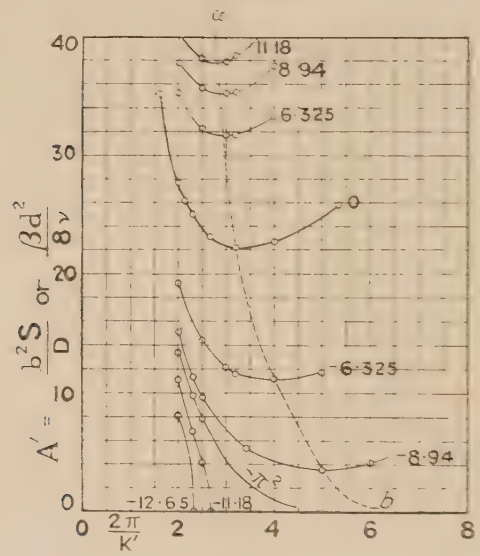
* 'Theory of Sound', i. §§ 88, etc.

† *Loc. cit.*, § 19.

‡ I am indebted to Miss S. W. Skan for carrying out the laborious calculations involved in this part of the work.

Appendix to this note: the results are exhibited in fig. 4, where the coordinates are the same as in fig. 2, but the contours all relate to conditions of neutral stability ($\alpha = 0$), under varying intensities of the tension T. The numbers attached to the contours are values of the non-dimensional quantity Tb^2/D: the particular values shown were chosen for convenience in calculation.

Fig. 4.



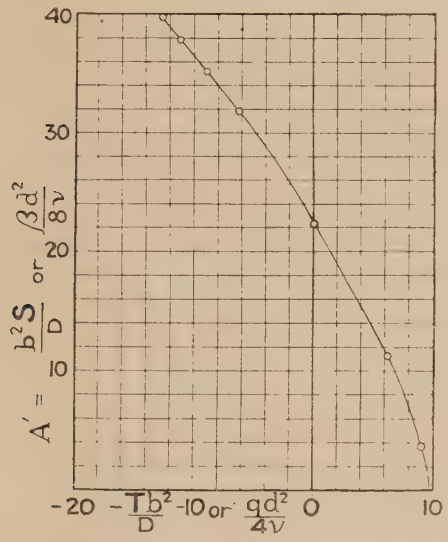
In fig. 4, the contour ($Tb^2/D = 0$) is identical with the contour numbered 0 in fig. 2. The contour numbered $-\pi^2$ is asymptotic to the horizontal axis; the contour for any (algebraically) higher value of Tb^2/D exhibits a minimum corresponding to a displacement of some finite wavelength; and the contour for any lower value cuts the horizontal axis orthogonally *. Thus for any contour value there is some lowest value of the ordinate b^2S/D, given by the point of intersection of the contour with the dotted curve *ah* of fig. 4; and a curve may be drawn (fig. 5) to relate the applied tension T with the minimum value of

* The complete diagram includes a part for negative values of the ordinate b^2S/D which may be obtained by reflexion of fig. 4 with respect to its horizontal axis. *Cf.* § 16 of the paper cited.

the shear which must be superposed in order that conditions of limiting stability may result.

If the constants of the strip are specified by (20), fig. 5 may be interpreted as a relation between β, q, ν and d; and this relation, by the argument of § 6, will give a lower value of β, corresponding to any specified values of q, ν and d, than can occur in a solution of the hydrodynamic equations of § 3. We see that the value of β, when ν and d are

Fig. 5.



specified, increases steadily as q decreases, and in particular, that instability of the steady shearing motion (q zero or negative: *cf.* § 3) cannot possibly occur unless β exceeds a value given by

$$\frac{\beta d^2}{8\nu} = 22{\cdot}18,$$

or

$$\frac{\beta d^2}{\nu} = 177, \text{ approximately,} \qquad (21)$$

which is the value obtained by substituting from (20) in equation (1). This is Orr's result (*cf.* § 3).

Conversely, when $\frac{\beta d^2}{\nu}$ has specified values, the curve of fig. 5 fixes lower limits for the value of the logarithmic

decrement q in the most persistent disturbance which can occur. These results are, so far as I am aware, new; but it should be emphasized that the fact of the curve extending to negative values of q does not necessarily imply that the steady shearing motion can become unstable for infinitesimal disturbances at any value of $\beta d^2/\nu$, however high.

Appendix.

Determination of Conditions of Neutral Elastic Stability for a Flat Strip subjected to Tension in combination with Shear.

Methods for deriving these conditions from fig. 2 of the present note were indicated in § 19 of the paper cited. Relations were there given whereby any set of simultaneous values for shear, frequency and wave-length which constitutes a solution of the equations of vibration under shear alone can be transformed into a new set of simultaneous values of shear, tension, wave-length and frequency which also constitutes a solution.

When, as in the present instance, the new frequency is required to be zero, the relevant transformation equations* are

$$\left.\begin{aligned} 2k'^2 + \frac{b^2\mathrm{T}}{\mathrm{D}} &= 2k^2, \\ \mathrm{A}'k' &= \mathrm{A}k, \\ k'^2\left(k'^2 + \frac{b^2\mathrm{T}}{\mathrm{D}}\right) &= k^4 - \mathrm{B}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (22)$$

where

$$\left.\begin{aligned} &\mathrm{T} \text{ is the tension per unit length, assumed equal in all directions,} \\ &l = \frac{2\pi b}{k} = \text{wave-length of the transverse displacement in a direction parallel to the edges,} \\ &\mathrm{A} = \frac{b^2\mathrm{S}}{\mathrm{D}}, \\ &\mathrm{B} = \frac{8\pi^2\rho h b^4 n^2}{\mathrm{D}}, \end{aligned}\right\} \quad . \quad . \quad (23)$$

and where undashed values of k and A relate to the original solution, dashed values to the new solution.

From the first and third of (22) we have

$$\mathrm{B} = \tfrac{1}{4}b^4\mathrm{T}^2/\mathrm{D}^2, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

* numbered (39) in the paper cited.

showing that if a new diagram (fig. 4) is constructed in which contours of constant tension are plotted against abscissæ representing $\frac{2\pi}{k'}$ and ordinates representing A′, then any contour of constant B in fig. 2 will transform into a contour of constant tension in the new diagram. Given the contour value b^2T/D, and assuming a value for k', we have B from (24) and k from the first of (22); then A may be found from fig. 2 and hence A′ from the second of (22), so that a point on the required contour is determined.

Fig. 4 has been constructed from calculations, made on the foregoing lines, which are summarized in the table given below. For our present purpose we are mainly interested in the lowest values of A associated with any given value of b^2T/D: these minimum values correspond to points on the dotted line *ab* of fig. 4, and are related with Tb^2/D in fig. 5.

It may be remarked that the complete diagram, extending to negative values of A, would exhibit symmetry about the horizontal axis: this follows from the fact that fig. 2 possesses a similar symmetry *. Hence, such contours in fig. 4 as intersect the horizontal axis will cut it orthogonally. The points of intersection are most easily found directly from the equation of neutral stability for a strip subjected to tension without shear; this is †

$$\left[\frac{d^2}{dz^2}-k'^2-\frac{b^2T}{D}\right]\left[\frac{d^2}{dz^2}-k'^2\right]Y=0, \quad . \quad . \quad (25)$$

and the boundary conditions require that ‡

$$Y=\frac{dY}{dz}=0 \text{ when } z=\pm 1. \quad . \quad . \quad . \quad (26)$$

To find the contour which is asymptotic to the horizontal axis of fig. 4 we make k' zero in (25). We thus arrive at the familiar solution

$$\text{with} \quad \left.\begin{array}{l} Y \propto (1+\cos \pi z), \\ \dfrac{b^2T}{D}=-\pi^2. \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

* *Cf.* § 16 of the paper cited.

† Equation (13), modified in accordance with § 19, of the paper cited.

‡ Equations (15) of the paper cited.

TABLE.

b^2T/D.	B in fig. 2.	k' (assumed).	k from (22).	A from fig. 2.	$A'=Ak/k'$.	$2\pi/k'$.
12·65	40	3·142	4·025	33·0	42·3	2·0
		2·513	3·558	28·3	40·0	2·5
		2·094	3·273	$25·5_5$	39·9	3·0
		1·967	3·192	24·8	40·2	3·2
		1·571	2·965	23·0	43·3	4·0
11·18	31·288 ...	3·142	3·930	32·2	40·3	2·0
		2·513	3·453	27·8	38·1	2·5
		2·094	3·159	25·2	37·9	3·0
		1·967	3·073	24·6	38·4	3·2
		1·571	2·839	22·9	41·4	4·0
8·94	20	3·142	3·787	31·4	37·9	2·0
		2·513	3·287	27·3	35·7	2·5
		2·094	2·976	24·9	35·3	3·0
		1·967	2·890	24·1	35·4	3·2
		1·571	2·634	22·4	37·6	4·0
$6·32_5$	10	3·142	3·610	30·7	35·3	2·0
		2·513	3·082	26·4	32·3	2·5
		2·094	2·748	24·2	31·7	3·0
		1·967	2·670	23·6	31·8	3·2
		1·571	2·373	$22·0_5$	33·3	4·0
$-6·32_5$	10	3·142	2·590	23·3	19·2	2·0
		2·513	1·781	20·3	14·4	2·5
		2·094	1·106	23·0	12·1	3·0
		1·967	0·841	27·4	11·7	3·2
		1·571	$0·834i$	$-21·0i$*	11·2	4·0
		1·257	$1·258i$	$-11·7i$*	$11·7_5$	5·0
−8·94	20	3·142	2·325	20·5	15·2	2·0
		2·731	1·729	18·0	11·4	2·3
		2·513	1·366	$17·8_5$	9·7	2·5
		1·837	$1·047i$	$-9·5i$*	5·4	3·42
		1·257	$1·700i$	$-2·7i$*	3·6	5·0
		1·047	$1·837i$	$-2·4i$*	4·2	6·0
$-\pi^2$	24·3	3·142	2·222	$19·3_5$	13·7	2·0
		2·731	1·589	16·8	9·9	2·3
		2·513	1·183	16·7	7·9	2·5
		2·059	$0·834i$	$-9·7i$*	3·9	3·05
−11·18	31·288 ...	3·142	2·070	17·0	11·2	2·0
		3·731	1·367	13·5	6·8	2·3
		2·513	0·863	$18·8_5$	4·1	2·5
		2·364	0	0	0	2·66
−12·65	4·0	3·142	1·833	13·8	8·3	2
		2·743	1·092	0	0	2·29

* A calculated from equations (24) of the earlier paper cited.

More generally, we have

$$Y = P \sin \alpha z + Q \cos \alpha z + R \sinh k'z + S \cosh k'z, \quad (28)$$

where

$$\alpha^2 + k'^2 + \frac{b^2 T}{D} = 0, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and the criterion is

$$2(1 - \cos 2\alpha \cosh 2k') = \frac{\alpha^2 - k'^2}{\alpha k'} \sin 2\alpha \sinh 2k'. \quad (30)$$

Inserting any value of k' in (30), we can find α by trial, and hence the value of $\frac{b^2 T}{D}$ from (29).

LVI. *The Disappearance of Gas in the Electric Discharge* (V.). *By* The Research Staff of the General Electric Company, Limited, London *. (*Work conducted by* N. R. Campbell *and* E. G. New.)

Summary.

The purpose of these experiments is to discover a relation between the rate of absorption of a gas in the electric discharge and the rate of ionization of its molecules. It is pointed out that the true electrical absorption, dependent simply on ionization or allied processes, is entangled with other causes of absorption and evolution of gas; the main difficulty is to disentangle it.

The experiments show that, in nitrogen and carbon monoxide, the rate of absorption is proportional to the rate of ionization and, approximately at least, independent of the pressure, the speed of the ionizing electrons, and the arrangement of the electrodes. It depends very greatly on the condition, but not very greatly on the material, of the walls of the vessel. The number of molecules disappearing is often greater than the number ionized. In argon there is no evidence of an absorption simply related to ionization. In hydrogen the facts are obscure; but it is probable that there is an electrical absorption more rapid than in N_2 or CO.

An attempt is made to explain the facts. In spite of the simple relation between absorption and ionization, it does not seem possible to hold that the ions are absorbed. Alternative theories are discussed: (1) that monatomic molecules liberated by ionization, (2) that partially ionized or excited molecules are absorbed; but both are open to grave objection. The molecules almost certainly are absorbed by reaction with the walls of the vessel, but no suggestion can be made as to the nature of the reaction.

* Communicated by the Director.

Some observations, to be completed in a later paper, are described on the evolution of gas from glass vessels when heated, after they have been submitted to the usual processes of baking during exhaustion. It appears that there is no definite amount of gas that can be evolved by such heating, but rather that an equilibrium pressure is established.

The paper consists of the following parts:—

§ 1–2. Statement of the Problem.
§ 3–4. Experimental Methods.
§ 5. General Nature of the Results.
§ 6–11. Detailed Results. Effects of anode voltage (6); Arrangement of electrodes (7); Nature of gas (8): Pressure of gas (9); Nature of walls (10); Thermal evolution of gas (11).
§ 12. Comparison with Previous Work.
§ 13–17. Discussion of Results. Absorption and ionization (13, 14); Absorption and monatomic molecules (15); Absorption and excited molecules (16); Nature of absorption (17).

Statement of the Problem.

1. In the previous papers of this series * we studied the disappearance of gas in the electric discharge, with special reference to the action of phosphorus. We put forward a theory to explain the specific effect upon the disappearance which phosphorus displays in common with certain other elements; and concluded that this effect was due to the formation of layers of chemically inactive phosphorus on the walls of the vessel; the gas appeared to adhere with particular avidity to such layers. But we did not offer any definite account of the circumstances which determine the adherence of the gas. If the disappearance is due to the electrical discharge, there should be some relation discoverable between the rate of disappearance on the one hand and, on the other, some quantities determining or determined by the discharge, such as the rate at which ions are formed, or at which they encounter the walls or other ions or neutral molecules, or the rate at which electrons strike the absorbing surface.

The experiments we are about to describe are concerned with this further problem. Since it appeared likely from

* Research Staff of the G. E. C.: Phil. Mag. xl. p. 585 (1920); xli. p. 685 (1921); xlii. p. 227 (1921); xliii. p. 914 (1922).

our previous work, confirmed in this respect by our preliminary survey of the new field, that the presence of phosphorus and its congeners would be a disturbing factor, we have made no use of these elements; nothing was intentionally present in the vessels we used, except glass, metal, and the gas which was to disappear. A thermionic cathode was always used, and its presence will be assumed in the sequel.

Some guidance could be obtained from the work of others, which has been summarized by Dushman in his book 'High Vacuum' and in the articles collected therein *. All writers find, as is to be expected, that the rate of disappearance of gas is proportional to the current carried by the discharge. Hughes † has compared the number of molecules disappearing with the number struck by electrons; he concludes that the ratio of these numbers is independent of the electron current, and that as many as one-sixth of the molecules struck may disappear. Dushman, Andrews, and Huthsteiner ‡ have shown that at constant pressure and electron current the rate of disappearance is proportional to the pressure. All these experiments, which will be discussed later, indicate that the rate of disappearance is proportional to the rate of ionization; but little definite is known of the factor of proportionality.

2. However, though quantitative measurements are scanty, qualitative facts, which have been published by many writers and are familiar to all who attempt to obtain very high vacua, indicate clearly the lines along which experiments should be directed. The problem is obviously complicated, because the true electrical absorption that we are trying to investigate is partially masked by several other causes of the evolution or disappearance of gas. These we will mention and discuss briefly in turn, in order to explain the nature of our experiments.

(1). There is the chemical absorption investigated so carefully by Langmuir. It is chiefly noticeable with hydrogen in the presence of hot metals (especially tungsten), and with gases which undergo an "ordinary" chemical reaction with the material of the vessel. Other gases, such as N_2 or CO, react with tungsten only when it is so hot that it has an appreciable vapour-pressure. This chemical absorption is easily distinguished from the electrical absorption,

* S. Dushman, General Electric Review (1920, 1921).
† A. Ll. Hughes, Phil. Mag. xli. p. 778 (1921).
‡ S. Dushman, General Electric Review, xxiv. p. 671 (1921).

because it takes place in the absence of the field; and it affects our experiments only in so far as it limits the choice of materials for investigation.

(2). There is an absorption of gas in or on new surfaces of the vessel, formed either by sputtering or by evaporation from some other part of it *. Part at least of this absorption is independent of any electrical action, although (as in the case of phosphorus) it may influence electrical absorption greatly. In such experiments as ours it must be avoided by using low potentials and comparatively low temperatures of the thermionic cathode, and thus reducing sputtering and evaporation.

(3). On the other hand, there is an evolution of gas which appears purely thermal and depends on the present state and past history of the vessel as regards temperature, and on the gas that has already disappeared in it. It is an obscure matter which we are still investigating and on which we hope to publish more later. We have only once (and that under unknown conditions) obtained a vessel in which the pressure did not increase regularly as the temperature was raised; and we have never obtained one in which the pressure would not increase slightly on standing at constant temperature after gas had disappeared in it. But this evolution can be reduced to a minimum by prolonged baking of the vessel at the highest permissible temperature and in the best possible vacuum before experiments begin; such precautions were always taken; the effect on our results of the residual evolution, which could not be eliminated, will be discussed later.

(4). There is an electrical evolution of gas independent of the thermal evolution, part at least of which has been traced to the impact of electrons upon surfaces charged with gas. There is evidence that the electron stream can drive off gas from the anode, even if it produces no appreciable rise in general temperature (see further, p. 562). It is perhaps to be expected that a similar evolution of gas should be produced by a stream of positive ions; for such evolution would be no more than an aspect of cathodic sputtering. As will appear later, it is much more difficult to produce direct evidence of such evolution or to disentangle it from the electrical absorption; but the available evidence indicates that it is not a material factor in our experiments.

* See S. Dushman, General Electric Review, xxiv. p. 439 *et seq.* (1921).

Experimental Methods.

3. The vessels in which the disappearance of gas was studied were usually triodes. The cathode was usually a tungsten filament, but a few observations were made with oxide-coated filaments made of platinum or platinum alloy by the Western Electric Company *. It was surrounded by a nickel-wire spiral, similar to the grid of a receiving valve; indeed, the parts used were actually derived from R–5-volt valves of the M.O. Valve Company. The third electrode was either a nickel cylinder surrounding the spiral, similar to the anode of such a valve, or a layer of silver covering partially or almost completely the surface of the glass bulb. The volume of the bulb was usually 150 c.c., but bulbs of 80 and 350 c.c. were also used; they were sometimes connected by side tubes to other vessels, and the total volume of gas of the apparatus thereby increased. Most of the experiments were made with 150 c.c. bulbs with the cylinder surrounding the spiral (Type A), or similar bulbs with the surface almost completely silvered (Type B). In one vessel of type B the silvered surface was replaced by a nickel gauze fitting closely to the glass. The absorption in this vessel was indistinguishable from that in those with the silvered surface.

The electrical circuit of the triode was that appropriate to its use as an ionization manometer. But it was found in the preliminary experiments that much more consistent results were obtained if, by a reversal of the usual practice in valves, the electrode of smaller area (the spiral) was made positive to the filament and the electrode of the larger area (the cylinder or the silvered wall) negative to the filament. The reason is to be found in the electrical evolution, already mentioned, arising from the impact of electrons on gas containing surfaces; the smaller the area on which they impinge, the smaller the evolution. This arrangement was adopted unless the contrary is stated. In order to avoid confusion, the negative electrode, receiving the positive ions, will be termed the "collector" and not the "grid"; the latter term suggests the electrode of small area, whereas the collector was usually the electrode of larger area.

V_a, the voltage between cathode and anode, ranged from 50 to 350 volts; V_g, the voltage between cathode and collector, was usually 2 volts; but the value of V_g, so long

* To whom we would express our thanks for their courtesy in supplying us with some of their wire.

as it was of the right sign, was quite without effect on the experiments.

The gas used in most of the experiments, and that assumed when no contrary statement is made, was nitrogen nearly free from argon. Other gases will be discussed later (§ 8). It was introduced through the liquid-air trap after baking and exhaustion of the vessel and just before it was sealed off from the pump. The initial pressure was usually about 0·001 mm.

The Measurements.

4. Measurements were made of the electron current flowing to the anode i_a (10^{-6} to 10^{-4} amp.), the positive-ion current flowing to the collector i_g (10^{-8} to 2×10^{-7} amp.) and the time t. The pressure is measured by i_g/i_a. If we write

$$p=\alpha\frac{i_g}{i_a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

α was independent of p, i_a, V_g within relevant limits of accuracy for most of the vessels. The mean free path of the electrons, calculated from α, was always greater than the largest dimension of the bulb, because the electrons oscillated to and fro before finally falling into the small anode; it also increased with V_a. α was determined for each vessel, each V_a, and, if necessary, for each pressure, by a calibration, direct or indirect, in terms of a McLeod *.

The results are best expressed in terms of the ratio between n_1, the number of molecules disappearing per unit time, and n_2, the number of ions formed in the same time. If there is no recombination, and the ions are all singly charged, while

$$n_2=i_g/\epsilon, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$n_1=-\mathrm{NV}\frac{dp}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where N is the number of molecules in unit volume of the gas at unit pressure and room temperature, V the volume of the vessel, and ϵ the charge on an electron.

Consequently

$$\frac{n_1}{n_2}=-\alpha\mathrm{VN}\epsilon\frac{1}{i_g}\frac{d}{dt}\left(\frac{i_g}{i_a}\right), \quad . \quad . \quad . \quad . \quad (4)$$

* A recent letter ('Nature,' 112, p. 651 (1923) has been interpreted as challenging the reliability of the McLeod. Of course it is perfectly reliable if care is taken to avoid the presence of vapours; but the precautions necessary for this purpose are not always realized.

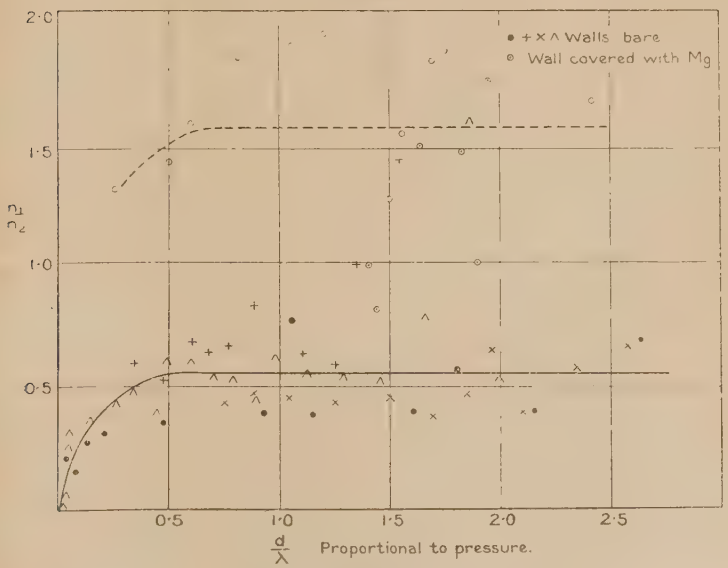
and all the quantities on the right-hand side can be measured. Again, in the expression of the results, it is best to replace the pressure by the ratio d/λ, where d is some length characteristic of the vessel and λ is the mean free path of one of the particles concerned; this ratio is, of course, proportional to the pressure. Actually d has been taken to be the greatest distance between anode and collector, λ the free path of the neutral molecule; d/λ will therefore be some measure of the number of collisions a positive ion is likely to make during its passage through the vessel.

No great precision was attempted in any of the measurements; for it was clear that sources of variation were present which would mask completely any mere experimental errors. But the absolute errors do not exceed 10 per cent.

General Statement of Results.

5. Fig. 1 shows the main features of the results obtained in a vessel of type A, n_1/n_2 being plotted against d/λ.

Fig. 1.



Typical Absorption Curve.

Curves of this nature will hereafter be termed "absorption curves." The points other than the circles show the results of four independent experiments, between which the vessel was opened, re-pumped, and re-filled with gas. These four

experiments agree with each other about as well as any similar set that has been made. They define quite certainly the general form of the curve represented by the solid line ; but the departure of individual points from that line is so great that a larger number of observations is necessary to arrive at any quantitative conclusions. Each of the four experiments shown requires about 8 hours' continuous observing ; it will be realized, therefore, that the experiments are exceedingly laborious, and that it is not a simple matter to secure measurements which will answer all the questions which may be raised.

There are three features of the curve to which attention should be directed :— (1) At the higher pressures, n_1/n_2 is nearly independent of the pressure; but (2) at lower pressures it decreases rapidly with the pressure, and tends to zero. (3) The constant maximum value of n_1/n_2 is not much less than 1. These three features are characteristic of all the observations that have been made with nitrogen. In some cases the distribution of the experimental points is so irregular that it would have been impossible to decide from these points alone even the general shape of the curve ; but the constancy of the form, whenever it was definite, together with the absence of any evidence in favour of any other form, appears to us conclusive. The only doubt that we have is whether the straight part of the curve is really horizontal ; there was sometimes an indication of a small constant increase of n_1/n_2 with the pressure.

The circles illustrate other important features characteristic of all our experiments. These measurements were made on the same vessel as the remainder ; but just before filling the vessel with gas, the collector cylinder was heated by electron bombardment, and a small quantity of magnesium metal attached to it was thereby evaporated and deposited on the glass walls of the bulb ; the metal film so formed was insulated during the observations and had no appreciable influence on the nature of the discharge. In this experiment the results of this process were two. In the first place the points become very irregular; indeed, they are as irregular as in any experiment we have made not open to suspicion ; they are given for that reason. The dotted line is drawn of the form shown, only because, as has been said, the general evidence indicates that this form is universal. But this is purely accidental. We have never been able to decide why some experiments are so much more irregular than others, and there is no evidence that such deposition of a metal on the walls tends either to produce or to remove

irregularity. In the second place the values of n_1/n_2 are increased, and are now in general greater than 1. This is not accidental. We have always found that the value of n_1/n_2 is largely determined by the treatment of the walls of the vessel, and that it is increased by any change (such as very prolonged baking or the deposition of a new film) which is likely to produce a surface relatively free from adherent gas. Further, we always find that, when such a surface is produced, the constant maximum value of n_1/n_2 is greater than 1.

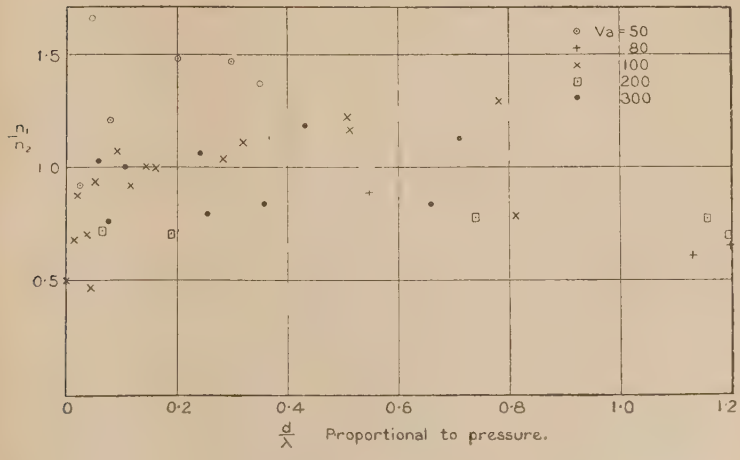
After this preliminary survey to indicate the points to be investigated, we will proceed to a more detailed account of the facts. Experiments have been directed chiefly to the influence upon n_1/n_2 of (1) the nature of the discharge, (2) the nature and quantity of the gas, (3) the nature of the walls.

Detailed Results.

Anode Voltage.

6. Our first question is whether n_1/n_2 is independent of the means by which the ionization is produced. Is it independent of V_a, which determines the speed of the ionizing electrons, and of the arrangement of the electrodes?

Fig. 2.



Variation of $\frac{n_1}{n_2}$ with V_a (Vessel B).

The effect of V_a was investigated by repeated experiments in the same vessel, in each experiment a pair of values of V_a being compared. Fig. 2 shows the results, the different

kinds of points referring to different voltages. It is clear that n_1/n_2 is greater with $V_a=50$ than with higher values. But these points are unreliable ; for with such a low value of V_a, a study of the relation (1) showed that the positive-ion current was not saturated, and that all the positive ions were not arriving at the collector ; some were disappearing by recombination. n_2 is consequently greater than i_g/ϵ, and the values of n_1/n_2 calculated from (4) are too high. For the remaining values of V_a, from 80 to 300 volts, there is no evidence of a dependence of n_1/n_2 on V_a ; the points seem to lie on two distinct curves, but each curve includes points with high and low values of V_a. It may be concluded, therefore, that the speed of the ionizing electrons within these limits has no very great effect on the rate of absorption, so long as the number of ions formed is the same.

This result has a subsidiary importance. If, as suggested on p. 556, there were an electric evolution, of the nature of sputtering, due to the impact of the positive ions on the collector, it should increase rapidly with V_a, and consequently the apparent value of n_1/n_2 decrease with V_a. Since no rapid variation is found, it may be concluded that if there is an appreciable evolution of this kind, it is not similar to sputtering.

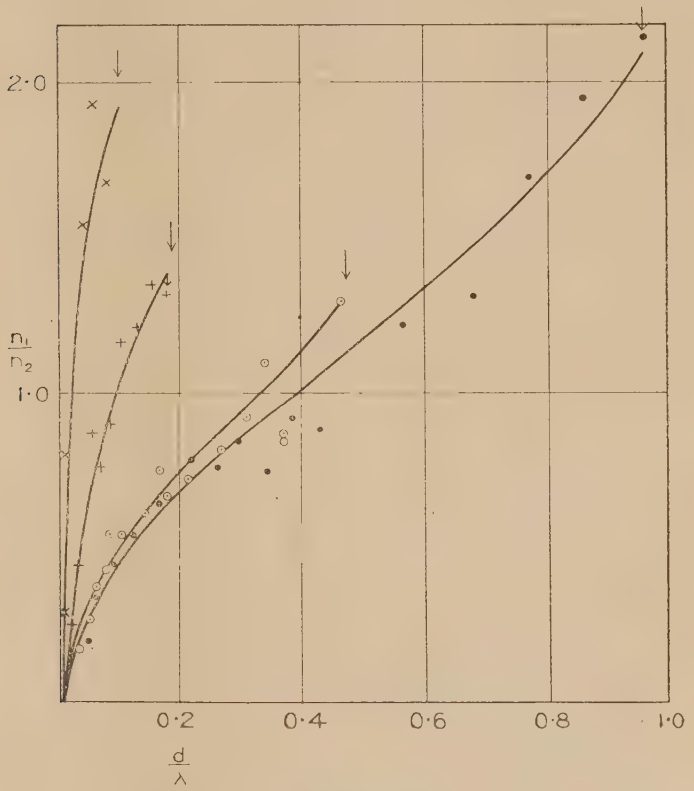
Area of Electrodes.

7. Another method of varying the nature of the discharge is by changing the disposition of the electrodes. In the earlier experiments the electrodes were connected as in a valve, the larger electrode being the anode. Fig. 3 shows the results of some experiments with this arrangement in a vessel of type B, the wall, silvered almost completely, being the anode. The curves are totally different from those of fig. 1 ; n_1/n_2 increases continuously with the pressure. Moreover, the disposition of the curve varies with the initial pressure (indicated by the arrow) ; n_1/n_2 initially is approximately the same whatever the initial pressure ; but the higher the initial pressure, the less is the value of n_1/n_2 at any lower pressure.

The reason for this difference has already been suggested ; it appears at once if experiments are made alternately with the large electrode as collector and as anode. If it is first made the collector, and some portion of the gas is absorbed, and if it is then made the anode, the immediate result of the discharge is an increase in pressure ; after a time the increase ceases and is replaced by a decrease, which gives a value not very different from that obtained in the previous

observations with the large electrode as the collector. If the connexions are reversed once more and the large electrode made collector, there is no appreciable increase, but absorption begins immediately with a value of n_1/n_2 not very different from that obtained originally.

Fig. 3.



Absorption Curves with Large Electrode as Anode.

It seems clear, therefore, that the impact of electrons upon the large electrode can liberate from it gas which has been absorbed by the discharge (and probably gas adherent to it from any other reason); the electronic current liberates gas from the large electrode, and not (to the same extent at least) from the small, simply because there is more gas adhering to the large electrode. The continual decrease of n_1/n_2 when the discharge is run continually with the large electrode as anode, is due to the continual increase in the

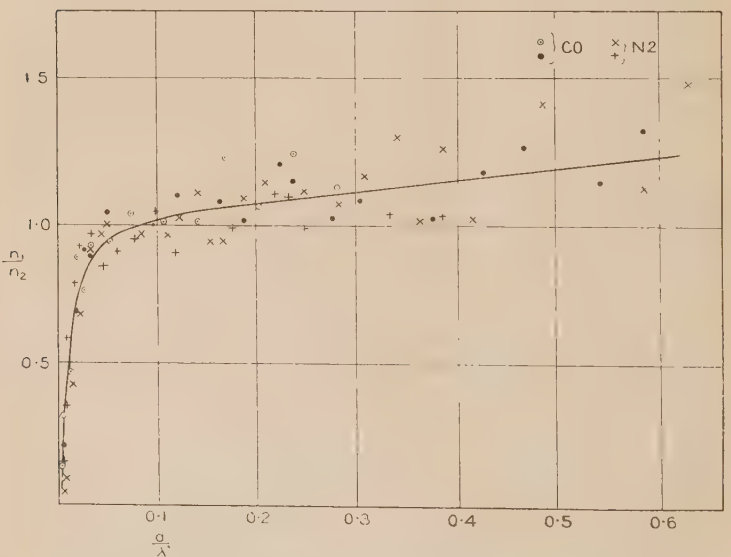
amount of gas absorbed on it and, consequently, in the rate of evolution counteracting the absorption.

There seems no doubt that this explanation is correct in outline; and, if that be so, experiments with the large electrode as anode are not likely to lead directly to a solution of our main problem. But there is one curious feature which suggests that there are further complications. In the experiments when the two arrangements of the electrodes are used alternately, the greatest value of n_1/n_2 when the large electrode is the anode is consistently greater than the greatest value when it is the collector; it may be nearly twice as great. To this matter we shall return in the discussion.

Various Gases.

8. The only other gas in which results closely similar to those for nitrogen were obtained is carbon monoxide, which

Fig. 4.



Absorption of CO and N_2.

was introduced into the vessel by bombarding a nickel anode in an attached vessel. Fig. 4 shows the results of successive experiments in the same vessel with this gas and with nitrogen. There is no certain difference between the two gases. An attempt at a closer comparison was made by

introducing the two gases into the same vessel without opening it and repumping, the nitrogen in this case being liberated by breaking a bulb ; the attempt was unsuccessful for a reason to be mentioned later.

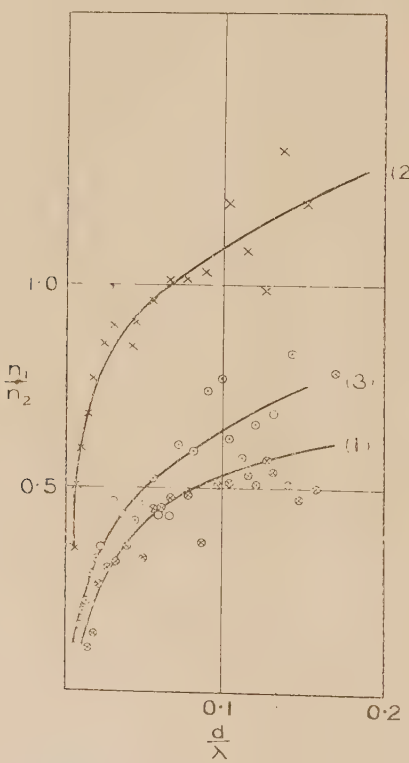
Measurements were made in argon. Here no definite absorption could be obtained of the same order as that in nitrogen ; n_1/n_2 was always less than 0·1. This result is contrary to that of Dushman, Huthsteiner, and Andrews (*loc. cit.*), who found that argon was absorbed at half the rate of nitrogen. But it is not clear that sputtering was avoided in their experiments. Argon and other inactive gases can certainly be made to disappear if considerable sputtering is in progress ; but we have not been able to satisfy ourselves that it will disappear, like nitrogen, in virtue of ionization and in the absence of appreciable sputtering.

Attempts were also made to investigate hydrogen and oxygen. With these gases a tungsten cathode cannot be used ; it was replaced by an oxide-coated cathode. Experiments with nitrogen showed that in this gas the measurements were quite independent of the nature of the cathode, a very complete comparison being obtained in a vessel provided with a tungsten cathode at one end and an oxide cathode at the other. No trace was found of the abnormal clean-up described by Hughes (*loc. cit.*). In oxygen there was complete failure, for the pressure of the gas changed when the cathode was heated in the absence of any field. The changes were complex, and were not always in the same direction. The matter has not been investigated further, for the changes were so large compared with any practicable rate of absorption due to ionization that it was clearly impossible to attain the main object of the experiment. In hydrogen there is also a change of pressure due to the mere heating of the cathode ; as Hughes has found (*loc. cit.*), the pressure decreases, as it does in the presence of hot tungsten, but much more slowly. It was possible, therefore, to obtain conditions in which the disappearance of gas proceeded far more rapidly when the gas was being ionized by the application of the anode voltage than when it was not. If it is assumed that the two processes of absorption are independent, then the experiments showed that n_1/n_2 for hydrogen was considerably greater than for nitrogen ; it was about twice as great. But the observations were not very regular, and the assumption on which their interpretation is based is by no means certain. The general form of the absorption curve is

probably not quite the same as in nitrogen, the straight part of the curve being inclined upwards, as in fig. 5 below.

Before any of these pure gases had been tried, a great number of preliminary experiments had been made with "residual gas" either left in the vessel by stopping the pump for a suitable period before sealing off or liberated

Fig. 5.



Residual Gas in Large and Small Vesssels.
(1) and (3), Small Vessels. (2), Large Vessels.

after sealing off by baking (see p. 571). The experiments were less regular than in nitrogen, but in the best series of experiments, shown in fig. 5, some consistency was obtained; the significance of the different curves in this diagram will be stated later. Here it seems clear that the straight part of the curve is not horizontal, but that there is a continual increase of n_1/n_2 up to the highest pressures observed.

However, owing to great irregularities in the earlier experiments, the curves were not carried so far as those taken later.

The question of course arises what is the nature of this "residual gas." Attempts were made to identify it by determining its ionization and resonance potentials, and comparing them with that of known gases in the same vessel. The method is not very accurate at pressures of a few thousandths of a millimetre; but the results indicated strongly that the gas is carbon monoxide. However, the difference in the shape of the curves of figs. 4 and 5, which seems real, suggests that it is not pure carbon monoxide, though no critical potentials which could be associated with another gas could be found. Hydrogen is the most probable admixture. On the other hand, if hydrogen is present it should disappear in the presence of hot tungsten without ionization by a field; but no change of pressure could be detected unless the field was applied. It is possible that carbon monoxide favours the action of the walls in catalyzing the reverse reaction, converting atomic into molecular hydrogen *; but the matter cannot be cleared up for the present.

Effect of Pressure of Gas.

9. Another question which arises concerns the effect of the pressure of the gas present. It is answered partially by the form of the absorption curves already given, which show that there is a considerable range of pressure, at least in nitrogen and carbon monoxide, within which n_1/n_2 does not vary rapidly with the pressure. But there is a possibility that, when the pressure is so high that the free path of the ions is small compared with the distance between the electrodes, the relation changes its form; such a change is almost inevitable at some stage if, at the lower pressures, there is a steady increase of n_1/n_2 with pressure. The vessels used in these experiments were not suitable for measurements at pressures much higher than those shown; indeed, as we found in previous work †, it is always difficult at higher pressures to measure the number of positive ions formed; we cannot, therefore, answer this question definitely. But it is important, in order that our present work may be connected with that described in our earlier papers. In those papers the initial pressure was of

* See R. W. Wood, Phil. Mag. xliv. p. 538 (1922).
† Phil. Mag. xlii. p. 227 (1921).

the order of 0·1 mm., whereas now it is of the order of 0·001 mm. Is the process the same in the two cases? In reply, we can only point out that there appears to be perfect continuity between the two processes, and that such estimates as can be made, necessarily very rough, of n_1/n_2 at the higher pressures, indicate values certainly not much lower and possibly a good deal higher than those obtained at the lower. We believe that the two processes are essentially the same, but that complicating factors, to be discussed later, enter at the higher pressure.

Effect of the Walls.

10. Our observations in this matter may be summarized in the statement that the material of the wall is relatively unimportant, but (as might be expected) any treatment of the walls which tends to rid them of adherent gas or to prevent the evolution of that gas, produces at the same time an increase in the true rate of absorption (and not merely in the apparent rate).

Thus, prolongation of the baking and pumping in a very high vacuum increases the absorption, though a limit appears to be reached after which no improvement is possible. Bombardment of the electrodes by electrons has the same effect, quite independently of a liberation of gas from the body of the metal in virtue of increased temperature. Cooling the wall of the vessel in liquid air during the discharge again increases absorption, and all the gas absorbed is not liberated when the liquid air is removed. Lastly, the deposition of a film of any material on the walls while the vessel is evacuated increases absorption.

In this last observation we are clearly repeating the results that we described at length in our previous paper *, which was concerned with much higher pressures. Again, we have been unable to establish any connexion between the nature of the film deposited and the absorption; but the results are so capricious that we are not prepared to assert that there is no connexion. The materials we have tried are tungsten, magnesium, copper, silver, cryolite, glass, and phosphorus. In the case of phosphorus the effects are complicated by the action of the discharge on the deposited film, which is discussed at length in our earlier papers (*loc. cit.*). On the other hand, the conditions of deposition have a marked effect, especially the pressure obtaining in the vessel when the deposition occurs. If the pressure is too

* Phil. Mag. xliii. p. 914 (1922).

high before the evaporation is started, or if a considerable quantity of gas is liberated at the same time as the vapour of the substance to be deposited, then there is a marked decrease in absorption. If gas is present during the evaporation, some of it is always absorbed during the process, as Langmuir has proved in the case of tungsten ; and in some cases there appears to be a slow absorption without the discharge after the new film is deposited. Care was, of course, taken that the experiments on absorption by means of the discharge were not started until the pressure in the absence of the discharge was constant ; the increased absorption observed cannot be simply due to an effect independent of the discharge. But it may be asked whether the similarity found between all newly deposited films was not due to their being all actually covered with the same layer of absorbed gas. We are clear that they cannot have been completely covered, because in some cases the total quantity of gas which had access to the film between the evaporation and the starting of the absorption experiment was much less than that required to form a monomolecular layer over the whole surface.

The area of the walls appears also to affect the absorption, which is larger in the larger vessel. This point is illustrated in fig. 5, where the upper curve refers to a bulb of 350 c.c. volume, the lower pair to one of 70 c.c. volume. The two bulbs were in connexion, they contained the same electrodes, and the values of α were nearly the same. (When the spiral is used as anode, α does not depend greatly on the volume of the vessel.) The curves were taken in the order 1, 2, 3, gas being liberated after each experiment by baking the vessel. There is no doubt of the effect of volume, but the ratio between the absorptions is not so great as the ratio of the areas of the vessel.

The "fatigue" of the absorption was also investigated. For this purpose the absorption vessel was connected to another in which carbon monoxide could be liberated by the heating of a nickel anode. Successive portions of gas were thus introduced and absorbed. A progressive decrease in the rate of absorption was produced, each absorption curve being generally lower and beginning to fall away markedly at a higher pressure. The decrease of absorption became perceptible when a quantity of gas had been absorbed which would cover a tenth of the walls with a monomolecular layer ; the absorption became too slow to observe accurately, having fallen to about one-tenth of its original value, when a quarter of a monomolecular layer had been absorbed. It

was this fatigue which prevented the comparison of different gases by successive absorption in the same vessel (see p. 565).

Here it may be recorded that the greatest value of n_1/n_2 we have ever actually observed in a single observation is 13, and the greatest value constant over a considerable range of pressure 10·5. But there are doubts about these values. They were obtained in a vessel in which the collector was a squirrel-cage lamp filament, the anode being the usual spiral. The total area of the electrodes was therefore very small. In such conditions there is much doubt whether i_g measures the number of positive ions. There was a certain range of pressure over which α in equation (1) was constant; it fell off rapidly at lower pressures, indicating clearly that the positive ions were disappearing by recombination rather than by arrival at the collector. Over the constant range in which the experiments were made the proportion arriving at the collector must have been constant, but it is difficult to be certain that it was unity; and if it was not, the values of n_1/n_2 would be too high. Apart from this vessel, the highest value obtained was 2·5 on the flat part of a good curve; but higher values up to 5·4 were often obtained when the discharge was first started. The first few observations were often irregular, and usually above the remainder of the curve; what is their significance cannot be determined until the cause of variation is known.

The Thermal Evolution.

11. Closely connected with the influence of the walls is the evolution of gas when the vessel is heated. We have attempted to study this evolution in detail; if intelligible results could be obtained, they might give much information concerning the nature of the absorption. We propose later to report on these experiments more fully; at present the results are chaotic and unintelligible. But one important fact is clear. There is no definite amount of gas that can be liberated by baking; the results of increased temperature resemble rather the establishment of a vapour-pressure than the progress of a continuous reaction.

If a vessel exhausted for several hours while maintained at (say) 360° C. is sealed off, allowed to cool, and then maintained at (say) 100°, the pressure increases, rapidly at first and then more slowly, until after a period of many hours (say 100) an equilibrium pressure is attained which does not increase with time. If it is now cooled, the

pressure falls, rapidly at first and then more slowly ; the original pressure at room temperature is not usually reached ; there is some permanent evolution. If the heating and cooling are repeated, an equilibrium pressure, somewhat higher than before, is attained, and the final pressure reached on cooling is again somewhat greater. If, after the original heating at 100°, the temperature is raised to 200° C., the pressure will again reach equilibrium at a higher value. Permanent increases are produced by alternate heating and cooling; but there is some reason to believe that even this permanent evolution decreases as the cycle is repeated, and that finally a state would be obtained in which the equilibrium pressure is determined only by the temperature.

These features are characteristic of all the well-exhausted vessels we have examined (except one, wholly anomalous and unexplained, which gave no change of pressure with temperature), whether or not gas has been made to disappear in them by the process studied here. In fact, we have never been able to satisfy ourselves that the absorption of gas by the discharge had any effect on the thermal evolution ; it is certainly not true that, if two vessels are exhausted in apparently the same way and gas is absorbed in one and not in the other, that in which gas has been absorbed will always give the greater rise of pressure with temperature. In other words, we have no evidence that the gas absorbed by this process is capable of being restored by heating to any temperature under 300° C.

Nor does there appear to be any temperature below this limit at which the electrical absorption ceases; if the discharge is passed in the warm vessel absorption occurs, but at a smaller rate than at room temperature.

In the course of the experiments on "residual gas" many observations were made in which gas was alternately liberated by heating and absorbed by the discharge in the same closed vessel. On each repetition of the cycle the equilibrium pressure attained at any temperature during the baking decreased, and the value of n_1/n_2 at any pressure during the absorption increased. The cycle on the whole tended to remove gas. If the facts are to be represented in terms of vapour-pressure, the relation between thermal evolution and electrical absorption can be summed up in the statement that the discharge progressively decreases the vapour-pressure of the vessel.

Comparison with Previous Work.

12. Before discussing our results, it will be well to compare them briefly with those of Hughes (*loc. cit.*), who alone appears to have made measurements of the same nature. Hughes compared the number of molecules absorbed with the number of collisions between molecules and ionizing electrons, and not with the number of ions formed. With the anode voltages which he used, probably about one collision in every four resulted in ionization (see below, p. 578); accordingly his "b" will be comparable with our n_1/n_2 if the former is multiplied by 4. It then appears that the greatest value of n_1/n_2 which he observed was about 0·7. This is consistent with our results, for his vessel was very small; however, since the walls were cooled and under bombardment by electrons, and since he was using hydrogen, we should have expected him sometimes to observe higher values. He finds a progressive decrease of the rate of absorption with increase in the initial pressure, which is what we find when the anode forms a considerable fraction of the walls of the vessel. He finds more variation with the anode voltage than we do; but since his absorption was not nearly independent of the pressure, his observations on this point are not comparable with ours. He finds less difference between nitrogen and hydrogen than we find. We agree with his observations that there is no appreciable absorption unless there is ionization. We have found no trace of the anomalous clean-up which he found in nitrogen, but our vessels with oxide-coated filaments were not cooled in liquid air.

Discussion of the Results.

Absorption and Ionization.

13. We have now summarized those observations which we have been able to reduce to some kind of order; the proportion reducible to order would probably have been greater if a clue had been discovered earlier. An attempt to explain them must answer two main questions. The disappearance of the gas is doubtless due to some reaction between the molecules of the gas and of the solid walls, resulting in the formation of stable complexes attached to the walls. We have to determine what is the nature of this reaction and what is the state of the molecules of the gas which enables them to undergo this reaction. It is just possible that this second question does not arise, that the effect of the discharge is wholly on the walls, and that the

molecules of the gas which disappear are in their normal state ; but all the evidence seems against this view, and we do not propose to consider it further.

We shall start with the second question ; and we shall pay attention primarily to the absorption curves of the form shown in figs. 1 and 4 which are obtained with nitrogen and carbon monoxide. For though an explanation of these curves would not cover the whole ground, we feel convinced that they represent the phenomena in their simplest form, and that the other absorption curves involve complicating factors which are best left out of account in a preliminary survey.

At first sight, we might be inclined to adopt a very simple hypothesis. It might be supposed that ionization causes absorption, because the positive ions themselves adhere to the walls.

But this, the most natural theory, is open to the gravest objection. For if the positive ions disappear as positive ions, they must all disappear on the collector ; for the collector is the only solid surface they hit while they are positive ions ; when they leave it they are certainly uncharged, because their charge has passed through the galvanometer. This argument is unaffected if the ions never really take up an electron, but merely attract one to the surface of the electrode ; if the ion subsequently left the electrode, this electron would be set free in the electrode. But, from the time of the earliest experiments on this subject, all the evidence has been against the absorption of the gas on the electrode which received the positive ions ; it has always been much more probable that it is absorbed on any surface exposed, almost irrespective of its charge. To this evidence we have added.

In one experiment, the collector was a squirrel-cage lamp filament. After a considerable amount of gas had been cleaned up in this vessel, the collector was heated to more than 2000° K. for a few minutes, but no considerable fraction of the gas was restored. The small increase of pressure which occurred could well be attributed to the heating of the walls by the incandescent filament. Conversely, in other experiments a portion of the wall of the vessel was cooled in liquid air. An increase in n_1/n_2 was thereby produced, even if this part was the anode or was of bare glass and insulated. Again, in one vessel the wall of the vessel was silvered in two separate halves. Both halves were initially bombarded with electrons till no more gas was evolved. During the absorption of the gas, one of the halves

was kept at a small positive potential, the other was the collector and received all the positive ions. After the gas had been absorbed, one of these was made the anode of the discharge and bombarded with electrons; gas was then evolved (*cf.* § 7). If the gas had collected on the collector, the evolution should have been greater if that half was bombarded; but no difference between the two halves could be discovered.

Lastly, there are the experiments of § 7, when the small electrode was the collector. It would doubtless help to explain some of the facts if it could be supposed that the gas was always absorbed on the collector, and that the difference in the maximum absorption, according as the collector was the large or the small electrode, was due to a difference in the material of which they were composed. But the quantity of gas that could be absorbed with the small electrode as collector was far greater than would cover that electrode completely with a monomolecular layer of gas, whereas in the experiments of p. 569 the absorption practically ceased long before a monomolecular layer was completed. This difficulty is still more marked in the experiments with the lamp filament as collector; the area of this electrode was even smaller than that of the spiral surrounding the cathode. And the possibility that in this experiment all the positive ions were not reaching the collector makes the difficulty even worse; for, on the theory that we are discussing, if the ions do not reach a solid electrode, but are neutralized by recombination, they should not disappear.

None of these arguments is entirely conclusive by itself, but, taken together, they seem to us to make it almost impossible to maintain that the absorption of the gas is due directly to the absorption of the positively-charged ions. Alternative theories must be considered; but before proceeding to them, it will be well to notice some questions which will arise whatever theory is adopted.

The Form of the Absorption Curve.

14. First, is it certain that all the positive ions arrive at the collector? May not some part of the bare insulated glass be negatively charged and receive positive ions, which, perhaps, are continually neutralized by a small fraction of the electronic stream? We do not believe that there is any appreciable action of this sort. In vessels of type B, the bare glass was reduced to the minimum necessary for insulation, and its effect can hardly have been appreciable. Most of our results were obtained with vessels of this type,

and are therefore unaffected by the possibility suggested. Moreover, no material difference could be found between the observations in such vessels and in those of vessels of type A, where there was a large area of bare glass, or in those of type B with only part of the walls silvered. Again, the positive-ion current was always saturated and did not increase with V_g. Lastly, exploration of the charges on the bare glass by various methods showed that the surface of this glass was always very nearly at the potential of the cathode, and therefore less likely to receive positive ions than the negatively-charged collector.

Second, what is the significance of the form of the absorption curve, and how can values of n_1/n_2 occur which are greater than 1? If the theory that we have just discussed were true, n_1/n_2 could be greater than 1 only if the positive ions collected to themselves neutral molecules either before or after they were absorbed on the walls. The form of the absorption curve might suggest that the formation of complexes of primary positive ions and neutral molecules occurred before absorption, and that the rapid falling-off of the absorption at low pressures was due to a diminution of the frequency of collisions at which such formation can take place. But the falling-off occurs at pressures too low for this explanation to be probable; the curve is straight far below the pressures at which the chance of a collision between a neutral molecule and a positive ion on its way to the collector has begun to decrease rapidly. We believe that the form of the curve at the lowest pressures is due simply to the partial counteraction of the absorption by one or more of the evolutions discussed on p. 556. When the pressure becomes low, dp/dt necessarily falls unless i_a is very greatly increased; the ratio of the thermal evolution to the electrical disappearance is no longer inappreciable, and n_1/n_2 appears to decrease. Confirmation of this suggestion was sought in observations of the thermal evolution when the fields were removed and the discharge stopped; it is difficult to obtain great accuracy in the comparison, but in some cases at least the residual thermal evolution measured in this way was quite sufficient to account for the falling-off of the curve; again, the falling-off occurs at lower pressures when the thermal evolution is small. There is also the electrical evolution from the small anode to be taken into account. In a general survey of the observations we can find no evidence that, if all evolution could be suppressed, n_1/n_2 in nitrogen and carbon monoxide would not be nearly constant down to the lowest pressures.

If that is so, reactions between molecules of the gas, when they are in the gaseous state, cannot be responsible for the main part of the absorption of nitrogen and carbon monoxide. If reactions between gaseous molecules are a primary cause of absorption, they must take place between free molecules and those already condensed on the surface on the walls. On the other hand, if, in these gases, n_1/n_2 does increase slowly but regularly with the pressure (and we have never been able to decide whether it does or does not), this increase may be due to reactions between free molecules which play a secondary part in the absorption. In CO we know already of a reaction which might play such a part *. But even here the apparent decrease as the pressure falls may be due to the partial counteraction of the absorption by an evolution independent of the pressure, *e. g.* an electrical evolution from the anode of small area. In those gases, *e. g.* hydrogen and "residual gas," which show much more definitely a steady increase in n_1/n_2 with pressure, the influence of these reactions must be more important; but since, even here, they cannot be the sole cause of absorption, it is permissible and probably wise to discuss the matter first as if they did not occur.

Absorption and Monatomic Molecules.

15. But what alternative theories can be offered? If the particles of the gas are uncharged at the time of their absorption, the state which favours absorption must be one associated with ionization, but not ionization itself. An obvious suggestion is that the molecules are resolved by ionization, that in nitrogen and hydrogen the state in question is the monatomic state, and in carbon monoxide either the elementary state or some state of less saturated combination. But there are objections here also. Though it is certain that some molecules are resolved on ionization, it is equally certain that not all are. Our experiments on carbon monoxide (*loc. cit.*) indicated strongly that most of the molecules were unresolved; for nitrogen still more definite evidence is available from the interesting work of H. D. Smyth †. His results show that, when the speed of the ionizing electrons is below 350 volts, only about one-tenth of the ions are atomic; the rest are molecular. If, then, we are to explain the disappearance of more molecules than are ionized, we must suppose that the active atoms or

* Phil. Mag. xlii. p. 227 (1921).
† H. D. Smyth, Proc. Roy. Soc. A, civ. p. 121 (1923).

resolved molecules, after being absorbed, can collect around them other neutral molecules which happen to come into their neighbourhood. Such an action is not intrinsically improbable; but, if we have to account for values of n_1/n_2 at least equal to 3, while there is no evidence that the number of molecules primarily activated is more than a tenth of the ions, the magnitude of the complexes that must be involved in absorption become alarmingly large; at least 30 atoms must be concerned in them.

Further, if this theory is correct and Smyth's conclusions are reliable (as they appear to be), there should be a great increase in the value of n_1/n_2 when V_a is greater than 400 volts, because the ratio of atomic or molecular ions is greatly increased at such high voltages. The significance of Smyth's work for our observations was only realized when the experiments were nearly completed, and there has not been time to carry the observations of fig. 2 fully to higher values of V_a. But enough observations have been taken to show that there is no considerable difference between the values of n_1/n_2 at $V_a=300$ and $V_a=500$ such as would be expected if the resolution of the molecule were the determining factor in absorption. While, therefore, the evidence against this theory is not quite so strong as against the first which was noticed, the available evidence seems contrary to it; other alternatives must be investigated.

Absorption and Partial Ionization.

16. A third alternative is that the state of the molecules which favours absorption is excitation or partial ionization—that is to say, a quantum state higher than the normal but lower than ionization. There is much evidence* that excitation may favour the formation of complexes or definite chemical compounds, such as must be involved in the disappearance of material from the gaseous state. Moreover, the theory is not inconsistent with the values of n_1/n_2 that have been found or with their relation to V_a. If a vessel of type B is used with the silvered wall as anode, the distance travelled by the electrons is known approximately, and the average number of ions made by each electron can be compared with the number of collisions it must make if the dimensions of the molecules are taken from the kinetic theory. As the following table shows (in accordance with what is already known), the number of ions per collision is considerably less than unity, and does not vary very rapidly with V_a over the relevant range. If, as seems probable,

* See *e. g.* K. T. Compton, Journ. Opt. Soc. Amer. vii. p. 955 (1923).

every collision results either in excitation or ionization, the ratio of molecules excited to those ionized must be considerably greater than unity; it is therefore possible to explain the occurrence of values of n_1/n_2 greater than unity without introducing complexes involving more than one molecule of the gas.

V_a (volts).	Ions per collision.
100	0·179
200	0·208
300	0·236
400	0·257
500	0·271

But there are some difficulties. First, it is not possible to explain by the figures just given the highest values of n_1/n_2 observed. But there is some doubt about values greater than 3; moreover, they have always been observed when collisions between molecules of the gas were relatively frequent and the formation of complexes in the gas is not excluded. Second, perhaps the figures suggest a greater variation of n_1/n_2 with V_a than has been found. But here Smyth's results (*loc. cit.*) show clearly that the mere determination of ions per collision does not give full information as to the relative frequency of different types of ionization. Third, on this theory there should be some absorption when V_a is less than the ionization potential. We have never been able to detect such absorption; but since the absorption decreases rapidly with the voltage as the ionization potential is approached, it is just possible that it may have escaped detection. Last, the experiments of Wien and others* indicate that the duration of the excited state is of the order of 10^{-7} sec.; in such a period molecules excited throughout most of the vessel would not have time to reach the walls; and if they reach the walls in the normal condition, it is not easy to explain their disappearance. But perhaps this difficulty can be overcome by means of Compton's theory of the diffusion of radiation, and therefore of the excited state. The molecules that disappear may not be those originally excited, but those excited in immediate proximity to the walls by radiation due to the original excitation.

To sum up, the constancy of n_1/n_2 for variations of the pressure and of V_a, together with the absence of appreciable absorption when V_a is less than the ionization potential, suggests at first sight that the absorption of the gas is a direct consequence of ionization, and that the ions are absorbed. But this explanation seems impossible, because the ionized molecules remain ionized only during their

* W. Wien, *Ann. d. Phys.* lxxiii. p. 483 (1924), etc.

passage to the collector, and because they are not absorbed on the collector. Both the alternative theories are equally open to serious objections. The theory directly suggested by the facts is that molecules are absorbed when they have been ionized and subsequently neutralized by contact with the collector, that they are absorbed indifferently all over the surface of the vessel, and that after absorption they can collect round them neutral molecules and thus secure the absorption of more molecules than are ionized. But this theory is not easy to reconcile with what is known of ionization or atomic structure.

The Nature of Absorption.

17. The second problem to be solved by any complete theory is the nature of the reaction between the gaseous molecule and the wall which is the immediate cause of absorption. Here we have even fewer and less definite suggestions to offer The main difficulty arises from the apparent independence of the absorption of the chemical nature of the absorbing surface. If the absorption is "chemical," then whether it depends upon "primary" or "secondary" valencies, and whether it is more nearly allied to homopolar or heteropolar chemical combination, a definite influence of the material of the walls would be expected, and more difference than we have found between gases so chemically different as nitrogen and carbon monoxide. This last point is important; for even if it is thought that the absorption does not depend on the nature of the walls because it is really substantially the same in all gases (for instance, if they are always covered with a layer of gas), there is no doubt about the difference of the gas. It may be urged that a close similarity between nitrogen and carbon monoxide is to be expected if the absorption is purely "physical," and closely allied (*e. g.*) to the absorption by charcoal; but it may be replied that even here an influence of the nature of the walls is to be expected, and that the greater absorption of hydrogen and the far smaller absorption of argon show no analogy to this kind of absorption.

The only contribution that we can make to a solution is an indication that it is only a fraction of the whole surface of the vessel that can absorb. The experiments on fatigue show that the absorption decreases far more rapidly than the fraction of the surface that would remain uncovered if the absorbed gas were uniformly distributed. Again, the high values of the initial absorption in some experiments suggests that there is a part of the surface, soon used up, in an abnormally active condition. The special activity would

have to consist in an ability to absorb molecules less highly activated than those which adhere to the normal active surface. On the other hand, the recognition of inactive patches, and of the possibility that an activated molecule may not be absorbed because it strikes an inactive patch, increases the difficulty, already grave, of explaining values of n_1/n_2 greater than unity.

The influence of electron bombardment may provide a clue, though we cannot find it at present. It is easy to understand why such bombardment should liberate absorbed gas; for whatever may be the active state of the absorbed molecule, it is likely to be disturbed by the impact of electrons. But it is difficult to understand why the maximum absorption on a bombarded surface should be greater than on one that is not bombarded, and why such a maximum should occur between two stages in which the absorption is less than it is in the absence of bombardment. Unless it can be held that, when the small electrode is the collector, the gas is absorbed on that electrode piled up many molecules deep, it seems almost necessary to suppose that the absorption is different according as electrons are or are not striking the surface, and that the absorption which takes place in their absence is more easily reversed by the bombardment than that which takes place in their presence. But we can suggest no explanation of such a difference.

Finally, we would revert once more to the possibility of reactions between the molecules of the gas. It is highly probable that such reactions may occur; indeed, our previous work on carbon monoxide shows that in this gas they must occur; but it is highly improbable that the formation of complexes in such reactions is an important factor in absorption. To the reasons for this view that we have already given, we would add that positive ray analysis provides no evidence that complex molecules are often formed in the process of ionization; and that, even if they were formed in the gases that have been investigated, there is little likelihood that they would form solids and so cause directly the disappearance of the gas. On the other hand, if there is really a steady increase of electrical absorption with pressure in hydrogen (it is doubtful because of the absorption which takes place in the absence of the discharge), the normal molecules must be concerned in it in some way. If the theory of the absorption of excited molecules could be accepted, the effect of pressure might be attributed to secondary excitation due to radiation emitted under primary excitation. But the facts are here too uncertain to form the basis of any theory.

LVII. *The Dielectric Properties required for Maxwellian Radiation.* *By* A. Press *.

Summary.

QUITE apart from the two curl equations symbolizing Maxwell's Electromagnetic Theory, a consideration of generalized mechanics leads to a differentiation between the μ_r and k_r coefficients for radiant manifestations such as light or Hertzian waves on the one hand, and the μ_s and k_s coefficients for zero frequency conservative systems on the other hand. Indeed, the requirement is that in every case, as experiment shows, the k_s and μ_s coefficients should be larger. Then, taking note of Maxwell's curl equations it is proved that the electrical refractive index should not be expected to agree with the optically determined refractive index. The above two considerations necessarily lead to a modification of our concepts of self-induction and capacity coefficients for radiant systems.

The Activity Equations.

In a generalized mechanical system the activity A is defined as the result of multiplying the generalized force by a corresponding generalized velocity. In electrodynamics such force is the electrical intensity E, whereas the generalized velocity is the time-rate of change of generalized displacement D. Thus the activity per unit volume $d\tau = d\mathrm{N} \,.\, d\mathrm{S}$ is given by

$$\mathrm{A}_e = \frac{1}{d\tau}\left\{ E \,.\, d\mathrm{N} \,.\, \frac{dD}{dt} \,.\, d\mathrm{S} \right\} = E \,.\, \frac{dD}{dt},$$

with $d\mathrm{N}$ as the element of the unit normal N and $d\mathrm{S}$ as the element of area normal to N. Thus for a simple sinoidal variation of the quantities involved no real activity can possibly result if the generalized displacement D is taken to be in time phase with the impressed generalized force.

Consequences of Time-Variations Harmonically Considered.

For generality let it be assumed that :—

$$E = E_1 \sin pt + E_2 \cos pt,$$
$$D = D_1 \sin pt + D_2 \cos pt.$$

* Communicated by Prof. T. J. Schwatt, Ph.D.

Then we have that

$$A_e = p[\{E_2D_1\cos^2 pt - E_1D_2\sin^2 pt\} + (E_1D_1 - E_2D_2)\sin pt \,.\, \cos pt].$$

The term involving $\sin pt$, $\cos pt$ cannot give rise to any real time integrated activity, since the expression changes sign with the time. Yet by simple trigonometry the term $\{\}$ can be transformed, and then

$$A_e = p[(E_2D_1 - E_1D_2)_r \cos^2 pt + E_1D_2\cos 2pt + \tfrac{1}{2}(E_1D_1 - E_2D_2)\sin 2pt].$$

Whether any real activity results therefore depends on whether the expression $()_r$ is greater than zero or not. That is, for real consumption of energy the following inequalities must subsist :—

$$E_2D_1 > E_1D_2\,;\quad D_1/E_1 > D_2/E_2.$$

Indeed with

$$E_2D_1 - E_1D_2 = 0,$$

or what amounts to the same thing

$$E_1/D_1 = E_2/D_2,$$

there can only be a completely wattless consumption of energy. Thus for true radiation it is seen that the usual expression

$$D = kE$$

cannot obtain with k as a real (non-operational) number for the proportionality factor.

For the magnetic case equally and quite independently we must have, with

$$H = H_1\sin pt + H_2\cos pt$$
$$B = B_1\sin pt + B_2\cos pt,$$

that for real watt consumption

$$B_1/H_1 > B_2/H_2.$$

Therefore μ cannot be real but must be time-operationally complex.

Activity Requirements for Progressive Wave of Displacement Flux.

The inequalities above have been introduced to emphasize the time-phase factors only. A better form would be to set

forth the progressive and stationary wave-components of the generalized displacement. In this manner the radiant energy is localized in the voluminal displacement wave carried forward. Thus let

$$E = E_S + E_P,$$

where E_S is the stationary wave-component of force (as in a non-radiating condenser action) and E_P represents that component of the impressed force giving rise to the progressive (or radiant) wave-component. In the same way we have

$$D = D_S + D_P.$$

If now we set

$$\phi = f(x, y, z),$$

then it is proper to take

$$E = E_s \sin pt + E_p \sin (pt + \phi),$$
$$D = D_s \sin pt + D_p \sin (pt + \phi),$$

with the understanding that it is E_s that produces D_s, etc.

Investigating afresh the activity relations we find

$$A_e = (E_S + E_P)(dD_S/dt + dD_P/dt)$$
$$= \left(E_S \cdot \frac{dD_S}{dt} + E_P \cdot \frac{dD_P}{dt} \right) + \left\{ E_P \cdot \frac{dD_S}{dt} + E_S \cdot \frac{dD_P}{dt} \right\}.$$

It is evident that the terms in () can produce no real component of loss. With respect to the terms in $\{\}$ we have

$$\{\} = p[\cos\phi \cdot \sin pt \cdot \cos pt \,(E_p \cdot D_s + E_s \cdot D_p)_1$$
$$+ \sin\phi \cdot (D_s E_p \cos^2 pt - D_p E_s \cdot \sin^2 pt)_2].$$

By trigonometry, however, it again turns out that

$$()_2 = (E_p D_s - E_s D_p)_3 \cdot \cos^2 pt + E_s D_p \cdot \cos 2pt.$$

The real activity therefore depends on whether $()_3$ gives the following inequalities

$$E_p D_s > E_s D_p \; ; \; k_p = \frac{D_p}{E_p} < \frac{D_s}{E_s} = k_s,$$

and similarly for the magnetic case where with

$$H = H_s \sin pt + H_p \sin (pt + \psi),$$
$$B = B_s \sin pt + B_p \sin (pt + \psi),$$
$$H_s B_p < H_p B_s \; ; \; \mu_p = \frac{B_p}{H_p} < \frac{B_s}{H_s} = \mu_s.$$

Conceiving then, for convenience, of a new mathematical operator R such that when acting on the activity expression A_e it gives the real component of the energy rate consumption, we have

$$RA_e = p \sin \phi \,.\, (E_p D_s - E_s D_p) \cos^2 pt.$$

The latter expression can be transformed by means of the relations derived, and it follows :

$$RA_e = p \sin \phi \,.\, E_p D_p (E_s/E_p)(k_s/k_p - 1),$$
$$= p \sin \phi \,.\, E_p D_p (D_s/D_p)(1 - k_p/k_s).$$

For the magnetic case correspondingly we have

$$RA_m = p \,.\, \sin \psi \,.\, H_p B_p (B_s/B_p)\left(1 - \frac{\mu_p}{\mu_s}\right),$$
$$= p \,.\, \sin \psi \,.\, H_p B_p (H_s/H_p)\left(\frac{\mu_s}{\mu_p} - 1\right).$$

The magnitude of the radiation is therefore seen to depend on the relative strength of both fields stationary and progressive at any point. The above separate developments be it noted are quite independent of the two curl equations of Maxwell.

The Differential Equation of Maxwellian Radiation.—If the developed flux-coefficients are introduced into the expressions for the two displacement expressions, we have

$$D = k_s E_S + k_p E_P,$$
$$B = \mu_s H_S + \mu_p H_P.$$

Substituting the latter in the fundamental curl equations of Maxwell, we really have that

$$\text{curl } E = \text{curl } (E_S + E_P) = -dB/dt = -d/dt(\mu_s H_S + \mu_p H_P),$$
$$\text{curl } H = \text{curl } (H_S + H_P) = d/dt(D_S + D_P).$$

Assuming, for example, that the curl (line integral per unit of area) of dD/dt can be separated out into its two components independently, we have

$$\text{curl } H_S = dD_S/dt \;;\; \text{curl } H_P = dD_P/dt,$$
$$\text{curl } E_S = -dD_S/dt \;;\; \text{curl } E_P = -dB_P/dt.$$

In this manner, therefore, the following two resultant

equations will follow

$$\nabla^2 D_S = \mu_s k_s \frac{d^2 D_S}{dt^2}$$

$$\nabla^2 D_P = \mu_p k_p \frac{d^2 D_P}{dt^2}$$

Yet must we have

$$\mu_s k_s > \mu_p k_p,$$

which has important physical consequences.

Relation of Dielectric Constants to Index of Refraction.

It is a well-known fact from experiments with light waves for determining the index of refraction that the dielectric constant k always comes out smaller than when determined by the charged condenser method. Since light is a radiation phenomenon, and on the assumption of Maxwell it is electromagnetic, the value of the light velocity c is given by

$$c = \frac{1}{\sqrt{\mu_p k_p}}.$$

Yet for the electrical condenser experiments, where radiation effects are not emphasized, to say the least, it is not proper to take the right-hand term as $1/\sqrt{\mu_s k_s}$. The relative value of the refractive index i should be given by

$$i = \sqrt{\frac{\mu_p' k_p'}{\mu_p k_p}}.$$

The work of M. C. Gulton, *Comptes Rendus*, 1900, cxxx, p. 119, is therefore of exceptional interest. He found that the electrical refractive index for ice, for example, decreased progressively with larger and larger wave lengths, approaching more and more the value found by Fleming for a dry prism of ice when subjected to Hertzian waves. Quite a large table of values of i^2 and really k_s are given in Fleming's 'Principles of Wireless Telegraphy.'

Finally, it must be said that since the self-induction coefficient L, and the capacity coefficient C are dependent on the effective μ_s and k_s values, our conceptions of the constants are naturally altered in the light of the above inquiries. As for the power factor of an oscillating system, it is seen it must be always less than 50 per cent.

Chevy Chase, Md., U.S.A.
June 7, 1924.

LVIII. *Spectrophotometry of the Zeeman Effect in very weak Magnetic Fields.* *By* Wali Mohammad, *Ph.D.* (*Göttingen*), *M.A.* (*Punjab*), *B.A.* (*Cantab.*), *Professor of Physics, Lucknow University* *.

1. *Introduction.*

In order to study the distribution of intensity in a spectrum line when subjected to a very weak magnetic field and before the line is resolved into its components, the spectrophotometry of a photogram produced by an Echelon Grating Spectroscope was undertaken and the following arrangements adopted :—

2. *Source of Light.*

A source capable of giving sharp, fine, and bright lines is absolutely essential, and for this purpose an arc in vacuum produced by means of a Wehnelt oxy-cathode and an anode consisting of the given substance was used. The discharge-tube was similar to the one described previously by the author†, and consisted of a lime-coated cathode heated to incandescence by means of an electric current and an anode of zinc. A voltage of 220 volts was applied between the cathode and the anode, and the metal placed at the anode was made to evaporate and to emit light. This arrangement was virtually an arc in vacuum—the pressure being less than 0·01 mm. Hg. The zinc lines were chosen for investigation, as they had been proved to be without any satellites and had no complex structure and were sharply defined. By maintaining the current constant, the rate of the evaporation of the metal and consequently the intensity of the emission could be maintained uniform for considerable periods.

3. *Spectroscope.*

The spectroscope used was an echelon grating made by Hilger and consisted of 35 plates. This was used in conjunction with a monochromator of the constant deviation type. Its resolving power lies between 285,000 and 665,000 for the Fraunhofer lines A and H respectively, and the limit of the wave-length difference capable of being resolved is 0·027 and 0·006 Å respectively.

* Communicated by the Author.

† Wali Mohammad, Astrophysical Journal, xxxix. p. 185 (1914).

4. *Magnetic Field.*

The magnetic field was applied by placing the above mentioned discharge-tube containing the oxy-cathode and the anode between the poles of an electromagnet with adjustable poles, and capable of producing a field of about 7000 gauss when a current of 15 amp. was sent through it and when the distance between the poles was about 35 mm.

5. *Spectrophotometer.*

The photometer used was one constructed by Professor J. Hartmann *. In this instrument, the depth of tint at any point on the photographic plate is compared with that on a standard plate, and the place which has the same depth of tint is noted.

The instrument measures with high precision the density of a restricted area of the photographic image and can, with care and patience, be used to show the variation of this density from point to point.

6. *Sensitiveness of the Arrangement.*

Most of the Zeeman effect determinations have been made in very strong magnetic fields, and observations in weak fields are very few. The reason for this is obvious. The separation of the lines is so small as to require an instrument of very high resolving power to detect it. If the line is not a sharp one, its study offers further difficulties.

With the arrangement described above, the author not only detected but measured in the case of certain lines of cadmium the magnetic resolution in fields as weak as 300 gauss, and the author is not aware of any other measurements in fields much weaker than the above ; the lowest magnetic field in which the Zeeman effect appears to have been observed is 535 gauss, observed by O. V. Baeyer † by means of a Lummer-Gehrcke plate.

7. *Photograms.*

For photographing the lines Wratten and Wainwright's isochromatic plates were used, and several photographs were taken on the same plate in close proximity to one another. The magnetic field was gradually varied and was practically proportional to the current flowing in the coils, being 0, 290, 581, and 871 gauss respectively for currents of 0, 0·5, 1, and 1·5 amp.

* Hartmann, *Zeitschr. f. Instrumentenk.* xix. p. 97 (1899).

† Baeyer, *Verh. d. Deutsch. Phys. Ges.* viii. (1906) ; *ibid.* x. (1908).

8. *Sources of Error.*

Koch*, in an exhaustive study of the probable sources of errors in the photometry of spectrum lines, has mentioned no less than ten different sources, the most important among them being: the inhomogeneity of the photographic plate, the temperature variation during exposure, the diffusion of light in the photographic film, and the influence of the width of the slit. Apart from these there are other important sources of error likely to affect the experiments. These are :—

(*a*) The polarization impressed upon light which traverses fine slits. This phenomenon, originally noticed by Fizeau, has been further investigated by Zeeman †, who has shown that polarization caused by a too narrow slit gives rise to errors in determinations of intensity of components, and also to apparent shifts and dissymmetrical resolutions of spectrum lines with originally symmetrical distribution of light. He has shown that a quartz plate introduced before the slit of the spectroscope, giving a rotation of the plane of polarization of 45°, eliminates this source of error.

(*b*) The effect of the position of the echelon grating. The echelon grating may be used in either of the three positions :—

(1) When two neighbouring orders are of equal intensity.
(2) When only one bright single line is visible.
(3) Positions intermediate between these two with two lines visible but of unequal brilliancy.

By a slight rotation of the echelon about a vertical axis any of the conditions above mentioned can be secured, and therein lies the risk of changing the intensity of the lines and of getting dissymmetries.

The intensity curve of a fine spectrum line without a magnetic field shows the distribution to be quite symmetrical and similar to what may be expected on theoretical grounds. The agreement between the intensity curve observed by the author and that given by Koch ‡ in his researches on spectrophotometry is very close indeed. This shows that none of the above sources of error was present.

9. *Results.*

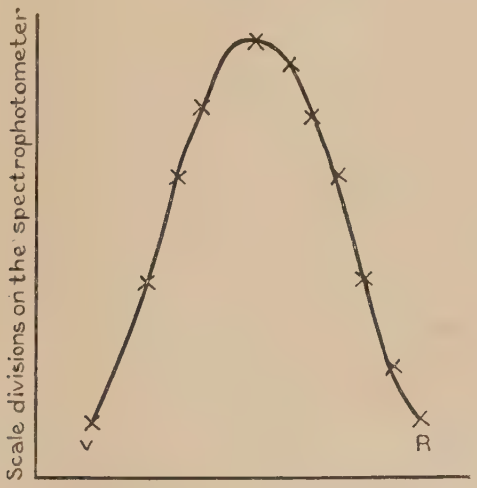
The red zinc line $\lambda = 6364$ was chosen for observation, and the curves of intensity variation in magnetic fields of varying

* Koch, *Annalen der Physik*, xxxiv. p. 377 (1911); xlii. p. 1 (1913).
† Zeeman, Proc. Roy. Acad. Amsterdam, xv. pp. 599–601.
‡ P. P. Koch, *Annalen der Physik*, xxxiv. p. 377 (1911).

strength are given. The line has been found to yield a normal triplet in the magnetic field. The middle component was removed by means of a Nicol's prism.

The curves show that even with the weakest magnetic field employed, the line shows two components not quite symmetrical either in intensity or in position, and this dissymmetry is maintained even when the field strength is increased.

Fig. 1.



Scale divisions on the microscope.

$H = 0$ Gauss.

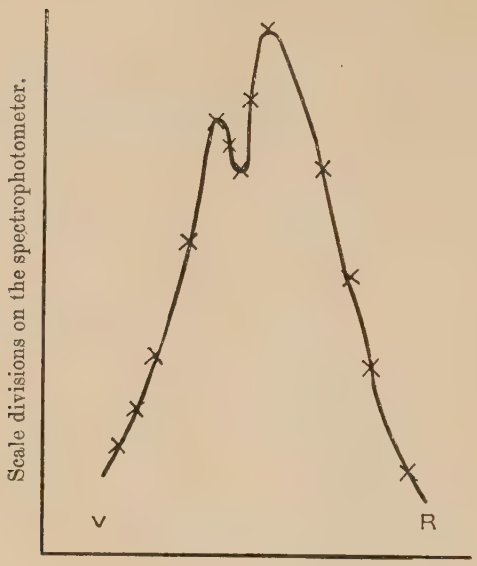
10. *Discussion.*

Not long after the discovery of the Zeeman effect and its explanation on the electronic theory of Lorentz, doubts were raised regarding the symmetrical distribution of intensity and distances of the components, and Zeeman and Voigt * predicted certain kinds of dissymmetries. According to Voigt normal inverse triplets in *weak* magnetic fields exhibit a dissymmetry of the following nature :—

The outer component on the side of the *red* has the greater intensity, and the component on the side of the *violet*

* Voigt, 'Magneto- und Electro-optik.' Voigt, Graetz's 'Handbuch der Elektrizität und des Magnetismus.'

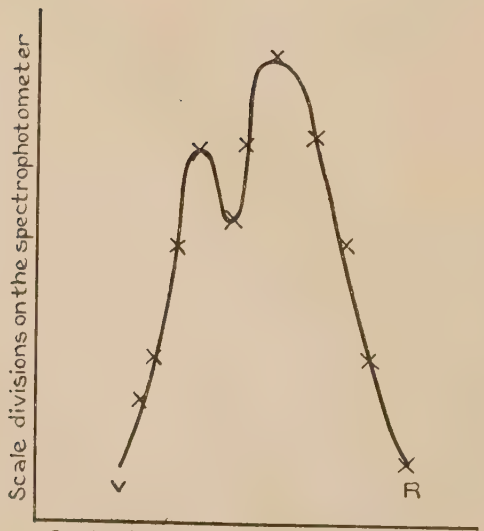
Fig. 2.



Scale divisions on the microscope.

H = 290 Gauss.

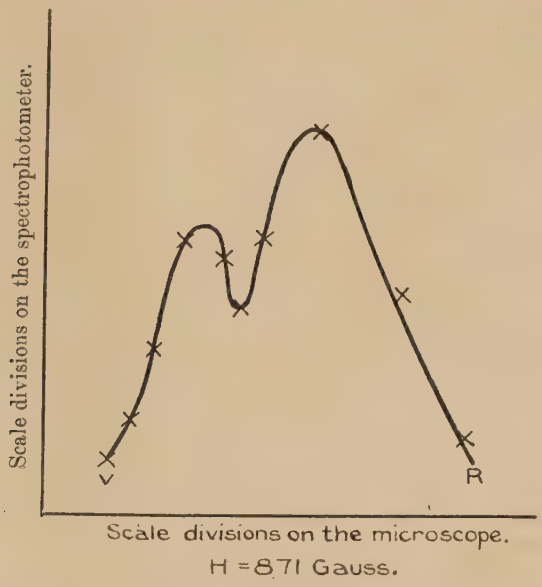
Fig. 3.



H = 581 Gauss.

will be at the greater distance from the original line. In weak fields, these dissymmetries will preponderate with observation perpendicular to the field, disappearing, however, in strong fields. Such dissymmetries have been proved to exist in many cases, and the spectrophotometric results given above appear to confirm the above-mentioned observations.

Fig. 4.



A dissymmetry of this nature cannot be explained on the simple electronic theory, but is probably due to one of the following causes :—

(*a*) It may be due to the coupling between electrons with different frequency. The interesting theory of the anomalous Zeeman effect developed by Voigt fully explains the sign and the nature of the dissymmetry observed above, and is probably the only theory put forward so far which not only explains the observed facts but even predicts phenomena which have later on been verified by observations. According to this theory, the displacements are proportional to the square of the strength of the magnetic field, but as the field becomes stronger the displacements tend to be proportional to the field strength. Moreover, the intensity of the component

on the side of the violet will be at a greater distance from the original line.

(*b*) It may be due to the modification of the quasi-elastic forces by the magnetic field, or a change in the structure of the radiating particles under the influence of the magnetic field. This view was adopted to explain the well-known Paschen-Back effect and was utilized by Voigt in developing his theory.

(*c*) The dissymmetry may be due to the interaction of the magnetic and electric forces. Zeeman * has proved experimentally, at least in cases investigated by him, that the magnetic force is solely responsible for a dissymmetry of such nature and that the electric force is not operative. It is true that such dissymmetries have been observed in flames where the electric forces are not operative, but there is no doubt that in an arc (or a spark) the conditions are certainly complicated and probably the Stark effect has something to do with such dissymmetries.

It may be remarked that the Bohr application of the quantum theory has not been able so far to explain some of the complicated but extremely regular magnetic resolutions. Sommerfeld, using Bohr's atomic model, has applied the quantum theory to account for the normal Zeeman effect, but he has neglected the squares of the magnetic field which are probably responsible for the dissymmetries of the kind noted above. He † has recently extended and simplified Voigt's classical theory, and Lande ‡, by making use of inner quantum numbers and energy levels, has tried to explain some of the observed facts. Yet the new theory does not take us any further, and more research is required before any satisfactory explanation can be found for these anomalous results.

* Zeeman, 'Magneto-optics,' p. 123.

† Sommerfeld, *Zeit. f. Physik*, viii. 257 (1922). Sommerfeld and Heisenberg, *Zeit. f. Physik*, xi. p. 131 (1923).

‡ Lande, *Zeit. f. Physik*, xi. p. 353 (1923).

LIX. *Some Notes on the Kinetic Theory of Viscosity, Conduction, and Diffusion.* *By* Prof. S. Chapman *and* W. Hainsworth, *B.Sc.**

§ 1. *The Conduction of Energy and Momentum by Rotating Molecules.*

THE most satisfactory treatment of viscosity and thermal conduction which has yet been given, for gases composed of molecules which possess *rotatory* as well as translatory motion, is that due to Dr. F. B. Pidduck †. This was based on the molecular model suggested by Prof. G. H. Bryan ‡, namely a sphere which is rigid, elastic, and perfectly rough. The condition satisfied by the motions of two such molecules immediately after collision is that the relative velocity of separation, for the points instantaneously in contact, is equal and opposite to the velocity of approach of these points just before contact occurs. Such a model effectively promotes interchange between translatory and rotatory energy, while preserving the indispensable mathematical advantages attaching to the spherical symmetry of the molecule.

Perhaps the most interesting of Pidduck's results are those which concern the ratio f, defined by

$$f = \frac{\lambda}{\mu C_v},$$

where λ is the thermal conductivity,

μ is the viscosity,

C_v is the specific heat at constant volume.

Theory and experiment agree in indicating that, for monatomic or non-rotating molecules, f is nearly equal to 2·5 §. Provided the molecule is spherically symmetrical and effectively smooth, so that it possesses no rotatory energy, the

* Communicated by the Authors.

† Pidduck, F. B., Proc. Roy. Soc. (A), vol. ci. (1922).

‡ Bryan, G. H., Brit. Assoc. Report, p. 83 (1894).

§ *Cf.* Chapman, S., Phil. Trans. A, ccxvi. pp. 279-348 (1915).

exact nature of the forces acting at encounters scarcely affects the value of f. For diatomic and polyatomic molecules, however, f is smaller and more variable: thus for hydrogen, nitrogen, and oxygen f is 1·90 or 1·91, for carbon monoxide and nitric oxide it is 1·88 and 1·86, for nitrous oxide it is 1·76, while for carbon dioxide and ethylene it is only 1·55 *.

Since viscosity represents a transference of momentum, and conduction a transference of energy, it is evident that the possession of rotatory energy diminishes the rate of transmission of molecular kinetic energy relative to that of momentum. The diminution is greater, moreover, the more the rotatory energy: in the above-named diatomic molecules the specific heats indicate that at ordinary temperatures the non-translatory energy corresponds to two degrees of freedom, the energy of any rotation which may occur about the axis of symmetry of the molecule being negligible, as the quantum theory would suggest; in the case of carbon-dioxide and ethylene, however, the non-translatory energy corresponds to more than two degrees of freedom, so that probably all three components of angular motion possess a share of the energy. Eucken † has shown that these values of f may be very fairly represented by the formula $\frac{1}{4}(9\gamma-5)$, where γ is the ratio of the specific heats; but this formula has no satisfactory theoretical foundation, and is moreover certainly too simple. Until Pidduck's paper appeared no numerically accurate calculations had been made for rotating molecules of a type even remotely comparable with actual molecules.

Pidduck found that with his model f is a function of the number K, where

$$\mathrm{K} \equiv k^2/a^2,$$

k being the radius of gyration and a the radius of the molecule. For a spherically symmetrical molecule K may range from 0 to 2/3 ‡, but f does not vary much with this change of K. For K = 0, 1/5, 1/3, and 2/3 the values of f are (to a first approximation) 1·85, 1·87, 1·85, and 1·71.

* *Cf.* Jeans' 'Dynamical Theory of Gases,' 3rd edition, p. 284.

† Eucken, *Phys. Zeits.* xiv. p. 324 (1913).

‡ Presumably by oversight, Pidduck takes K as varying from 0 to 1, which extends the range of his results beyond what is mechanically possible: K = 2/3 corresponds, of course, to the case when all the mass is concentrated at the surface of the sphere.

These differ but little from the observed values of f for *diatomic* molecules, and the correspondence may be regarded as giving theoretical support to Eucken's view. Diatomic molecules seem likely, however, to be less well represented by a spherically symmetrical model than polyatomic molecules like those of CO_2 or C_2H_4, for which Pidduck's values of f do not agree so closely with the observed values. It is therefore of interest to extend his work by taking a generalized form of his spherically symmetrical rotating model, embodying rather more accurately the properties of actual molecules. It is found that in this way the lower values of f may be accounted for, while the variation of λ and μ with temperature is also more closely paralleled. It is mathematically scarcely practicable to take the non-sphericity of diatomic molecules into account in calculating f; but Pidduck's results suggest that, as perhaps might be expected, the spheroidal form of such molecules enables them to transmute rotatory and translational energy into each other, during collisions, with the *maximum* efficiency which would be possible for any *spherical* molecule.

§ 2. *A Generalized Type of Rotating Molecule.*

The generalization of Pidduck's model which has been considered by us was suggested by the fact that, in the theory of a gas composed of *non-rotating* spherical molecules, any possible mode of interaction during collision may be treated mathematically as equivalent to elastic impact between rigid spheres, provided that the molecular diameter, instead of being taken as constant, is supposed to vary with the speed and directness of collision. The same idea may be applied to rotating molecules ; the radius of gyration k is supposed invariable, the change in the distance of closest approach being supposed to occur in the region beyond that in which the mass (represented by the positive nuclei in actual molecules) is distributed ; the collision-radius a is, however, regarded as variable, and as being expressed by

$$a = \sigma/x,$$

so that now

$$\mathrm{K} = k^2/a^2 = (k^2/\sigma^2)x^2 \equiv \mathrm{K}'x^2, \quad . \quad . \quad . \quad (1)$$

where σ is a constant, and x is a variable which may be a function of any invariant of a molecular encounter, other

than the total momentum. In the present case x was taken to be a function of the component (V) of the relative velocity of two colliding molecules, along the line of centres at impact. The function which was found most suitable for calculation is that which corresponds to the following formula for K (which by (1) is a multiple of x^2) :

$$\mathrm{K} = \frac{2/3}{1+\frac{b}{\mathrm{V}^{2s}}}, \qquad \ldots\ldots \quad (2)$$

where b and s are positive pure numbers characteristic of the type of molecule. If $s>0$, K increases with V, while the effective collision-radius (a) diminishes. The maximum value of K allowed by the formula is 2/3, in conformity with the condition of spherical symmetry ; clearly $\mathrm{K}=2/3$ when $b=0$ or $\mathrm{V}=\infty$. When $s=0$, K and x are constant, so that this special case coincides with Pidduck's model, different values of K corresponding to different values of b. The development of the theory, using this model, is closely analogous to that in Pidduck's case, which itself was a direct extension of the theory for non-rotating molecules*. The main difference in the final results is that certain integrals which occur in the expressions for λ and μ are analytically reducible only when $s=0$ (Pidduck's case), so that in the general case they have to be evaluated by quadratures.

The formulæ actually obtained as first approximations to λ and μ are as follows :

$$\lambda = \frac{3}{64\mathrm{K}'\sigma^2}\left(\frac{\mathrm{R}^3\mathrm{T}}{\pi m}\right)^{1/2} f_1(\mathrm{T}),$$

$$\mu = \frac{15}{32\mathrm{K}'\sigma^2}\left(\frac{m\mathrm{RT}}{\pi}\right)^{1/2} f_2(\mathrm{T}),$$

where T denotes the absolute temperature, m the molecular mass, and R the usual gas constant $1{\cdot}35\times10^{-16}$, while

$$f_1(\mathrm{T}) \equiv \frac{(\mathrm{I}_3+3\mathrm{I}_2)(12\,\mathrm{I}_1+25\,\mathrm{I}_2)-3(4\,\mathrm{I}_1\mathrm{I}_3-25\,\mathrm{I}_2^2)}{\mathrm{I}_2(4\,\mathrm{I}_1\mathrm{I}_3-25\,\mathrm{I}_2^2)}, \quad (3)$$

* Chapman, S., Phil. Trans. A, ccxvi. (1915), or Enskog, D., Inaugural Dissertation, Upsala, 1917, and *Arkiv f. Mat., Astron. o Fysik, Stockholm*, xvi. (1921).

where

$$I_1 \equiv \int_0^\infty e^{-g}\left\{\frac{13/4}{(1+K)^2}+\frac{g}{K(1+K)}\right\}dg,$$

$$I_2 \equiv \int_0^\infty e^{-g}\frac{dg}{(1+K)^2},$$

$$I_3 \equiv \int_0^\infty e^{-g}\left\{\frac{2+g}{K(1+K)^2}+\frac{2(1+2g)+3K(1+g)}{(1+K)^2}\right\}dg,$$

and

$$f_2(T) \equiv \int_0^\infty e^{-g}\left\{\frac{6Kg+6g+7K}{K(1+K)^2}\right\}dg. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$g = \frac{1}{4}\frac{m}{RT}V^2.$$

In terms of g, (2) gives

$$K = \frac{2/3}{1+b\left(\frac{m}{4RT}\right)^s g^{-s}};$$

so that the above integrals, and $f_1(T)$, $f_2(T)$, are functions of T unless $s=0$.

For comparison with Pidduck's work, values of $b\left(\frac{m}{4RT}\right)^s$ were determined for each of the values $s=0{\cdot}5$, $s=0{\cdot}7$, and $s=0{\cdot}9$ *, such that $\overline{K}$ should equal 1/5, 1/3, and 2/3, K being the mean of K averaged over all collisions. This leads to the formula :

$$K = \frac{2/3}{1+\frac{(2j-3)T_0^s}{3T^s g^s \Gamma(1-s)}}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where T_0 is the temperature at which $\overline{K}$ is to have the above values, while $j=5$, 5, or 3/2 according as $\overline{K}$ is equal to 1/5, 1/3, or 2/3.

The above formula, for the temperature T_0, gives the following values of f :—

K.	$s=0$.	$s=0{\cdot}5$.	$s=0{\cdot}7$.	$s=0{\cdot}9$.
0	1·85	1·61	1·48	1·25
1/5	1·87	1·66	1·50	1·29
1/3	1·85	1·70	1·58	1·47
2/3	1·71	1·71	1·71	1·71

* The integrals involved in $f_1(T)$ and $f_2(T)$ do not converge if $S>1$.

The first column ($s=0$) is a repetition of Pidduck's results. The values of f in the last row are constant because for $\bar{K}$ to equal 2/3 it is necessary that $b=0$, and therefore the model again reduces to (a special case of) Pidduck's model. The remainder of the table is new, and indicates that as s increases, corresponding to increasing "softness" of the molecule, the value of f appreciably diminishes. The theoretical range of f is thus extended in the direction required to explain the observed values of f for such gases as carbon dioxide and ethylene. This is as far as one can expect to go in the direction of theoretical explanation at present, in view both of the intrinsic analytical difficulties of the statistical theory and our almost complete ignorance of the nature of molecular interaction during collisions.

§ 3. *The Variation of Viscosity with the Temperature.*

The above generalization of Bryan's molecular model affords a better representation of the properties of actual gases in another respect, namely, in regard to the variation of viscosity and conductivity with temperature. Pidduck's results show that as long as the radius of the sphere is invariable (so that $b=0$, or $s=0$), λ and μ must be proportional to $T^{1/2}$, but our more general formulæ indicate that, when a varies with V, μ and λ also involve the factors $f(T)$ which are functions of temperature (*cf.* (3), (4), (5)). Their analytical expression is highly complicated, but the functions themselves are of simple form. One or two examples have been worked out to illustrate this.

Two values of s and three values of b have been considered; b has been chosen so that K_0, the mean value, averaged over all collisions, of the square of the ratio of the radius of gyration to the collision-radius (k^2/a^2) at the temperature 0° C., shall have the values 1/10, 1/5, or 1/3. For higher temperatures the value of K will be increased, because the radius of gyration, by hypothesis, remains constant, while with the greater molecular velocities the effective collision-radius will be decreased. The chosen values of s are 0·5 and 0·9, the greater value corresponding to the "softer" molecule.

With these data, it is found that the viscosity μ varies with absolute temperature T very approximately according to

the law T^n, over the range of temperature 0° C. to 250° C. (or 273° to 523° absolute). The values of n which give the best fit are given in the following table, which also illustrates the closeness of the fit, by including values of

$$\frac{\mu}{T^n} \Big/ \frac{\mu_0}{T_0^{n'}}$$

where the suffix 0 refers to 0° C. For T=273° or 0° C. this expression is unity, while the table indicates that in other cases its value differs extremely little from unity.

Adopted data.		Values of $(\mu/T^n)/(\mu_0 T_0^{n})$ for various temperatures.						Calculated.
$\bar{K}_0$.	s.	0° C.	50° C.	100° C.	150° C.	200° C.	250° C.	n.
0·10	0·5	1·000	1·002	1·002	1·001	0·999	0·997	0·86
	0·9	„	1·004	1·005	1·004	1·000	0·997	0·80
0·20	0·5	„	0·993	0·997	1·001	1·001	1·001	0·75
	0·9	„	1·000	1·000	0·998	0·995	0·990	0·68
0·33	0·5	„	1·002	1·003	1·002	1·001	0·998	0·67
	0·9	„	1·005	1·000	1·000	0·995	0·995	0·60

The values of n given in this table clearly increase as K diminishes and also as s diminishes. Since as s diminishes the molecule tends to Pidduck's case of the molecule of invariable size, it is at first sight surprising that n increases as s diminishes; but the reason for this is not improbably that, for such small initial values of K, the softer the molecule (or the greater the value of s) the more rapidly does $\bar{K}$ tend, with increasing temperature, to the value 2/3, another special case for which $n=1/2$.

The observed values of n exceed 1/2 for most known gases. For the diatomic gases hydrogen, oxygen, and nitrogen, n has the values 0·68, 0·74, and 0·78; while for carbon dioxide and ethylene it is 0·98 and 0·90. The above table does not quite cover this range of n, but indicates quite clearly that by taking $\bar{K}_0$ still smaller than 0·1 larger values of n can be arrived at. Moreover, these smaller values of $\bar{K}_0$ fit in well with the small observed values of f which correspond to gases like CO_2 and C_2H_4, for which the observed n is greatest. Thus the allowance for the "softness" of actual

molecules extends the theory of viscosity and conduction in gases whose molecules possess rotation, in the direction required in order to explain the observed facts.

§ 4. *The Definition of Temperature.*

A further point to which attention may be drawn relates to the definition of the temperature T in the non-uniform state of the gas.

Let C denote the *peculiar* velocity of a molecule, *i. e.* its velocity relative to the mean motion at the point; then $\frac{1}{2}m\mathrm{C}^2$ is the translatory kinetic energy of a molecule relative to the mean motion. Let E denote the total kinetic energy of a molecule, namely, $\frac{1}{2}m\mathrm{C}^2$ together with any energy of rotation or oscillation which the molecule may possess. Let N denote the number of degrees of freedom of the molecule: for "monatomic" molecules $\mathrm{N}=3$, for diatomic molecules $\mathrm{N}=5$, while for the molecules considered in this paper $\mathrm{N}=6$. If there is equipartition of energy between the various degrees of freedom,

$$\overline{\mathrm{E}}/\mathrm{N} = \tfrac{1}{2}m\overline{\mathrm{C}^2}/3,$$

where the bar above E and C^2 denotes that mean values are referred to. It is assumed in Pidduck's and the present work that this relation is satisfied in the steady state of the gas. It is not to be expected, however, that it will exactly hold good when the temperature or mean motion of the gas is not uniform. Hence the temperature of the gas will be reckoned differently according as one or other of the definitions

$$\tfrac{1}{2}\mathrm{NRT} = \overline{\mathrm{E}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\,a)$$

or

$$\tfrac{3}{2}\mathrm{RT} = \tfrac{1}{2}m\overline{\mathrm{C}^2} \quad . \quad . \quad . \quad . \quad . \quad (6\,b)$$

is adopted. The latter is the one used by Jeans in his 'Dynamical Theory of Gases,' while Pidduck adopts the former; the two methods agree, of course, as applied to the steady state of the gas. Jeans's procedure seems preferable, however, because it preserves the validity of the important relation

$$p = n\mathrm{RT},$$

connecting the hydrostatic pressure p with the number density (n) and the temperature of the gas; this follows from the fact that

$$p = \tfrac{1}{3}nm\overline{C^2}$$

whether the state of the gas is steady or unsteady.

The first approximation, F_0, to the velocity-distribution function, F, in the unsteady state is always taken to have Maxwell's form, which in the case of non-rotating molecules is

$$F_0 = n\left(\frac{m}{2\pi RT}\right)^{3/2} \exp.\left(-\frac{E}{RT}\right),$$

where E is the molecular energy as defined above, and n is the number density. According as T is defined by (6 *a*) or (6 *b*), it will follow that the integral of either

$$(F-F_0)E \quad \text{or} \quad (F-F_0)\tfrac{1}{2}mC^2$$

over all the molecules in any small volume must vanish. The latter relation implies that the *correct* hydrostatic pressure is obtained from the velocity-distribution function by using the first approximation; in the former case, however, this will not be so. This is not manifest in Pidduck's work, owing to the omission of a certain term in the additional expression (F_1) which, with F_0, gives the second approximation to F. The second approximation to p derived from the corrected form of F is

$$p = nRT\left\{1 + \frac{1}{128\pi^{1/2}K'n\sigma^2 I_2}\left(\frac{m}{RT}\right)^{1/2}\frac{D\rho}{Dt}\right\},$$

where $\dfrac{D\rho}{Dt}$ is the rate of change of ρ in a small volume moving with the gas. The additional term in p is of small magnitude, but it seems better not to introduce it at all, as is assured by taking (6 *b*) as the definition of temperature.

§ 5. *The Coefficient of Diffusion.*

It may be noted that the additional term in p does not vanish when K is equated to zero: this is not surprising when it is remembered that at the same time the angular velocity of the molecules must tend to infinity, if equipartition is to be maintained.

The first approximation to the coefficient of viscosity, however, reduces to the form appropriate to non-rotating molecules when K is equated to zero ; and the same is true for the first approximation to the coefficient of diffusion (D_{12}). The latter, which is not given by Pidduck, has been worked out, and may be quoted here :

$$D_{12} = \frac{3}{64\sigma_0^2 n_0 K_0' I_5}\left(\frac{2RTm_0}{m_1 m_2 \pi}\right)^{1/2},$$

where

$$m_0 = m_1 + m_2, \quad m_0 K_0 = m_1 K_1 + m_2 K_2,$$

$$\sigma_0 = \tfrac{1}{2}(\sigma_1 + \sigma_2), \quad n_0 = n_1 + n_2,$$

$$\frac{K_1}{K_1'} = \frac{K_2}{K_2'} = \frac{K_0}{K_0'} = x^2,$$

and

$$I_5 = \int_0^\infty e^{-g}\left\{\frac{K_1 K_2(1+g) + K_0 g}{K_0(K_0 + K_1 K_2)}\right\} dg.$$

For Pidduck's model this reduces to

$$D_{12} = \frac{3}{64\sigma_0^2 n_0}\left(\frac{2RTm_0}{m_1 m_2 \pi}\right)^{1/2} \frac{K_0 + K_1 K_2}{K_0 + 2K_1 K_2}.$$

§ 6. *Thermal Diffusion* : *Non-rotating molecules.*

The formula for the first approximation to D_T, the coefficient of thermal diffusion, in the case of *non*-rotating molecules, is

$$D_T = \frac{15 n_1 n_2 RT}{4 n_0^2 \Omega \Delta}\left\{\frac{a_{10}a_{1-1} - a_{11}a_{0-1}}{n_1 m_2^{1/2}} + \frac{a_{1-1}a_{-10} - a_{10}a_{-1-1}}{n_2 m_1^{1/2}}\right\},$$

where

$$a_{10} = \tfrac{1}{2}\mu_2^2 m_1^{1/2},$$

$$a_{-10} = -\tfrac{1}{2}\mu_1^{3/2}(\mu_2 m_1)^{1/2},$$

$$a_{00} = (m_1 m_2 \mu_1 \mu_2)^{1.2},$$

$$a_{11} = \left\{\sqrt{2\mu_2}\frac{\sigma_1^2}{\sigma_0^2}\frac{n_1}{n_2} + \mu_2\left(\tfrac{55}{4}\mu_1^2 + 19\mu_1\mu_2 + 12\mu_2^2 - \tfrac{25}{2}\mu_1 - 15\mu_2 + \tfrac{25}{4}\right)\right\},$$

$$a_{1-1} = a_{-11} = -\tfrac{27}{4}(\mu_1\mu_2)^{3/2},$$

while a_{-1-1} is the same as a_{11} with the suffixes 1 and 2

interchanged. Also

$$\mu_1 = \frac{m_1}{m_0}, \quad \mu_2 = \frac{m_2}{m_0},$$

$$\Omega = 16\left(\frac{2\mathrm{RT}\pi}{m_0\mu_1\mu_2}\right)^{1/2}\sigma_0^2,$$

$$\Delta = \begin{vmatrix} a_{-1-1} & a_{-10} & a_{-11} \\ a_{0-1} & a_{00} & a_{01} \\ a_{1-1} & a_{10} & a_{11} \end{vmatrix}.$$

The second approximation to D_{12} is given by

$$\mathrm{D}_{12} = \frac{3\mathrm{RT}}{2n_0\Omega\Delta}(a_{-1-1}a_{11} - a_{1-1}^2).$$

These differ somewhat from the values formerly given by one of us* ; the error, due to an oversight in algebra, was pointed out by Enskog †. The correction affects various numerical calculations which Chapman has given relating to thermal diffusion, but the error is fortunately of little importance. In the following special cases, these approximations to D_{12} and D_T and their ratio k_T take the forms :

(i.) $\dfrac{m_1}{m_2} \longrightarrow \infty$, $\sigma_1 = \sigma_2$.

$$\mathrm{D}_{12} = \frac{3}{64n_0\sigma_0^2}\left(\frac{2\mathrm{RT}}{m_2\pi}\right)^{1/2}\frac{4\sqrt{2}n_2 + 13n_1}{4\sqrt{2}n_2 + 12n_1},$$

$$\mathrm{D}_\mathrm{T} = \frac{15n_2}{256n_0^2\sigma_0^2}\left(\frac{2\mathrm{RT}}{m_2\pi}\right)^{1/2}\frac{n_1}{\sqrt{2}n_2 + 3n_1},$$

$$k_\mathrm{T} = 5\frac{n_2}{n_0}\frac{n_1}{4\sqrt{2}n_2 + 13n_1}.$$

(ii.) $\dfrac{m_1}{m_2} \longrightarrow \infty$, $\dfrac{\sigma_1}{\sigma_2} \longrightarrow \infty$.

$$\mathrm{D}_{12} = \frac{13}{256n_0\sigma_0^2}\left(\frac{2\mathrm{RT}}{m_2\pi}\right)^{1/2},$$

$$\mathrm{D}_\mathrm{T} = \frac{5n_2}{256n_0^2\sigma_0^2}\left(\frac{2\mathrm{RT}}{m_2\pi}\right)^{1/2},$$

$$k_\mathrm{T} = \frac{5n_2}{13n_0}.$$

* Chapman, Phil. Trans. A, ccxvii. pp. 166–185.

† *Arkiv f. Mat., Astron. o Fysik, Stockholm,* xvi. (1921).

The approximate value of k_T when $n_1=n_2$ is readily found to be 0·134 in case (i.) and 0·192 in case (ii.). It may be recalled that k_T is a measure of the difference of concentration of the gaseous constituents in two bulbs connected with one another by an open tube, but maintained at different temperatures*.

The following tables, correcting those in the works already referred to, illustrate the order of magnitude of k_T in other less special cases:—

(iii.)† (*a*) Argon-Helium. $\frac{m_1}{m_2}=9{\cdot}8$, $\frac{\sigma_1}{\sigma_2}=1{\cdot}69$.

$$k_T=\frac{5}{2n_0}\left\{\frac{0{\cdot}289n_1+0{\cdot}210n_2}{2{\cdot}165+1{\cdot}895n_1/n_2+0{\cdot}449n_2/n_1}\right\}.$$

(*b*) Oxygen-Hydrogen. $\frac{m_1}{m_2}=16$, $\frac{\sigma_1}{\sigma_2}=1{\cdot}34$.

$$k_T=\frac{5}{2n_0}\left\{\frac{0{\cdot}204n_1+0{\cdot}177n_2}{1{\cdot}630+1{\cdot}320n_1/n_2+0{\cdot}405n_2/n_1}\right\}.$$

(*c*) Oxygen-Nitrogen. $\frac{m_1}{m_2}=16/14$, $\frac{\sigma_1}{\sigma_2}=0{\cdot}97$.

$$k_T=\frac{5}{2n_0}\left\{\frac{0{\cdot}038n_1+0{\cdot}041n_2}{3{\cdot}689+1{\cdot}777n_1/n_2+1{\cdot}905n_2/n_1}\right\}.$$

The following table gives the numerical values of k_T for special cases of the above formulæ:—

n_1/n_2.	k_T.		
	(*a*).	(*b*).	(*c*).
1/3	0·139	0·140	0·010
1	0·138	0·142	0·013
3	0·097	0·086	0·010

* "A Note on Thermal Diffusion," Chapman and Dootson, Phil. Mag. xxxiii. p. 248 (March 1917).

† Phil. Trans. A, ccxvii. p. 185.

(iv.)* (*d*) Carbon dioxide and hydrogen. $\frac{m_1}{m_2}=22, \frac{\sigma_1}{\sigma_2}=\frac{1{\cdot}64}{1{\cdot}18}$.

$$k_T=\frac{5}{2n_0}\left\{\frac{0{\cdot}183n_1+0{\cdot}139n_2}{1{\cdot}292+1{\cdot}182n_1/n_2+0{\cdot}292n_2/n_1}\right\}.$$

(*e*) Sulphur dioxide and hydrogen. $\frac{m_1}{m_2}=32, \frac{\sigma_1}{\sigma_2}=\frac{2}{1{\cdot}18}$.

$$k_T=\frac{5}{2n_0}\left\{\frac{0{\cdot}182n_1+0{\cdot}102n_2}{0{\cdot}968+0{\cdot}166n_2/n_1+1{\cdot}201n_1/n_2}\right\}.$$

The following table gives the calculated values of the percentage difference of composition for the gas in the two bulbs used in Dootson's experiments (*l. c.*), together with the values experimentally obtained. The reason for the discrepancy is that referred to in § 7.

		Percent. difference of composition for the two bulbs.	
	No. of experiment.	Experimental value.	Calculated.
(*d*)	(1)	3·6	8·1
(*d*)	(2)	1·8	6·9
(*d*)	(3)	2 8	7·6
(*e*)	(5)	3·5	9·3

(v.)† (*f*) Ethylene and nitrogen. $\frac{m_1}{m_2}=1, \frac{\sigma_1}{\sigma_2}=\frac{2{\cdot}39}{1{\cdot}84}$.

$$k_T=\frac{5}{n_0}\left\{\frac{0{\cdot}068(n_1-n_2)+1{\cdot}040n_0}{233{\cdot}856+118(1{\cdot}277n_1/n_2+0{\cdot}757n_2/n_1)}\right\}.$$

The following numerical values of k_T are calculated from this formula.

n_1/n_2.....	1/3.	1.	3.
k_T	0·0091	0·0110	0·0075

§ 7. The above results refer to molecules typified by smooth elastic spheres of constant diameter: k_T is at its greatest for molecules of this type, while it vanishes altogether if the molecules are point centres of force varying inversely as

* "A Note on Thermal Diffusion," p. 252.

† "The Partial Separation by Thermal Diffusion of Gases of Equal Molecular Weight," Phil. Mag. xxxiv. p. 146 (August 1917).

the fifth power of the mutual distance r. The following table illustrates the approximate value of k_T for intermediate laws of force r^{-q}, and also indicates to what extent the first approximation to k_T is in error: this calculation is possible because by a method due to Lorentz an exact evaluation of k_T (and various other gaseous characteristics, including λ and μ) can be made when, as in case (i.), to which the present table refers, $m_1/m_2 \to \infty$, $\sigma_1/\sigma_2 \to \infty$. The exact formula for k_T is found to be

$$k_T = \frac{n_2}{n_0}\frac{q-5}{2(q-1)},$$

while by the general method the first approximation to k_T for this case is given by

$$k_T = \frac{5n_2}{n_0}\left(\frac{q^2-6q+5}{13q^2-42q+45}\right).$$

q	k_T (first approx.).	k_T (exact).
5	0	0
7	0·155 n_2/n_0	0·167 n_2/n_0
9	0·222 ,,	0·250 ,,
13	0·283 ,,	0·333 ,,
17	0·311 ,,	0·375 ,,
33	0·350 ,,	0·438 ,,
∞	0·385 ,,	0·500 ,,

It is clear that the error of the first approximation increases and becomes quite considerable as the case $q=\infty$, corresponding to molecules which behave like rigid elastic spheres, is approached.

(*g*) The most accurate experiments on thermal diffusion which have yet been made are those by Mr. T. L. Ibb*.

In an appendix to Ibb's paper, Chapman compared certain of Ibb's results with the theoretical formula. These results gave the *difference* of concentration of the two gases carbon dioxide and hydrogen in connected bulbs maintained at different temperatures, as a function of the mean relative proportion of the two gases. The corrected theoretical formula for this mixture has been given above, and the

* "Some Experiments on Thermal Diffusion," Proc. Roy. Soc. ser. A. xcix. no. A. 700, p. 385.

values of k_T for various mean relative concentrations of the two gases are :

Percent. SO_2.	Percent. H_2.	k_T calculated.
10	90	0·105
20	80	0·152
30	70	0·168
40	60	0·166
50	50	0·152
60	40	0·130
70	30	0·103
80	20	0·071
90	10	0·037

These figures do not differ much from those previously given, but it is satisfactory to find that the revision brings the values into even closer agreement than before with Ibb's observed data.

Summary.

(*a*) Pidduck's theory of viscosity and thermal conduction in polyatomic gases (*i.e.* gases possessed of rotatory as well as translatory energy) is generalized with the aid of a molecular model which takes account of the varying distance of closest approach between molecules depending on their relative speed of impact. The calculated values of the ratio f (§ 1), and of the variation of viscosity with temperature (§ 3), are thus brought into closer agreement with the observed results for various diatomic and polyatomic gases.

(*b*) The definition of temperature in the non-steady state of a polyatomic gas is discussed (§ 4), and it is pointed out that the definition used by Jeans is preferable to that used by Pidduck, since it avoids the introduction of an additional term in the usual expression for the hydrostatic pressure.

(*c*) A formula for the coefficient of diffusion appropriate to a polyatomic gas is given (§ 5).

(*d*) Revised formulæ and tables for various quantities connected with thermal diffusion in a monatomic gas are given (§§ 6, 7) correcting values previously published.

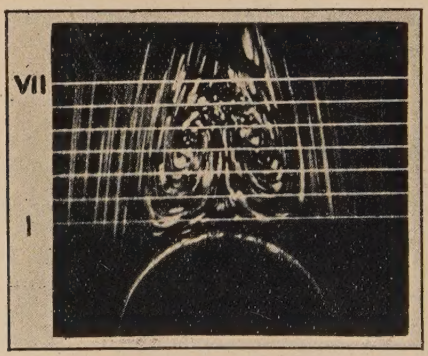
LX. *Eddies in Air.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I SHALL be glad if you will publish the following corrections to the paper on Eddies in Air (vol. xlvi. Nov. 1923, p. 754).

The name of my colleague was Hisamitu Nisi, and not as given inadvertently at the head of the paper.



The actual figure from which the measurements in the case of the cylinder were made is given herewith; the one shown as fig. 11, though also for a cylinder, was not the one utilised.

Yours faithfully,

ALFRED W. PORTER.